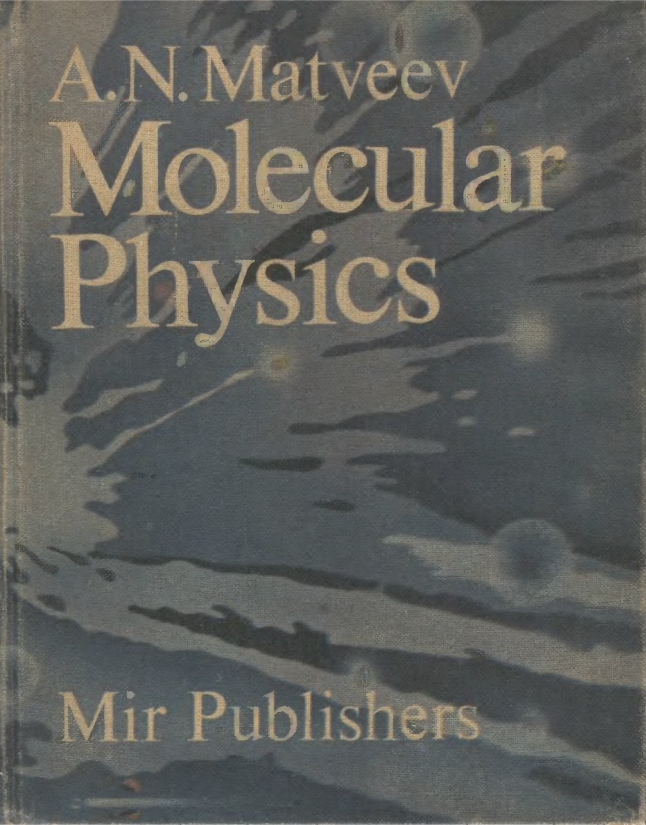




A.N. Matveev

Molecular Physics

Mir Publishers

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А. Н. Матвеев
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Preface

Molecular physics studies the molecular form of motion, i.e. the motion of large aggregates of molecules. Here two aspects of the problem are equally important: (1) the investigation of the molecular form of motion itself and (2) mastering the methods for studying many-particle systems and the concepts associated with them. The second aspect is not confined just to its application to the molecular form of motion. However, it is expedient to familiarize ourselves with the basic concepts of statistical physics and thermodynamics as applied to molecular systems since these systems are the most abundant in everyday practice. This is an important methodical argument. Many problems are difficult to study not in view of their complexity but since they are not encountered in everyday life which is the source of physical concepts of space and time. For example, it is assumed that classical mechanics is simple and quantum mechanics complicated. However, the problem of inertia is undoubtedly more complicated in its essence than the problem of quantization, and it is not less difficult to understand why two bodies cannot occupy the same volume in space than why two fermions cannot have the same set of quantum numbers.

Earlier, when molecular physics was established as a part of physics curriculum, the main attention was paid to studying the molecular forms of motion itself. Later, the emphasis was shifted mainly toward the study of statistical laws and the thermodynamic method as applied to molecular systems. In this case, the molecular form of motion becomes a particular case illustrating general regularities. The university courses for students were appropriately modified in the light of these trends. This textbook also adheres to these trends.

The book also contains material not covered by traditional courses but required for solving a wider range of problems than just the study of the properties of molecular systems. In the first place this applies to the electron and phonon gases. Although this material does not necessarily form a part of the existing curriculum, it is recommended as an optional reading since it gives the student a better idea about the distribution in the statistical description of phenomena.

From the relative merits of quantum and classical concepts discussed above it follows that quantum-mechanical concepts must be invariably introduced whenever the opportunity to do so is provided by experimental material. Naturally, we mean not the quantitative solution of a quantum-mechanical problem but the interpretation of experimental results with the help of quantum-mechanical concepts. For example, when the classical theory of the heat capacity of an ideal gas is studied, the experimental temperature dependence of the heat capacity of molecular hydrogen is as convenient for this purpose as the results of the Stern-Gerlach experiments in atomic physics.

Another important circumstance necessitating the application of quantum concepts is the requirement of a fairly rigorous substantiation of statistical physics. This can be done only with the help of quantum-mechanical concepts. It is natural to associate the entropy with the thermodynamic probability and the quantum (discrete) nature of a state. It is also important from a purely methodical point of view. The student is well aware that the general course of physics is not preliminary course which will be refined at a later stage. Rather, it is a comprehensive course in modern physics within whose framework lies the solution of many problems.

This book is based on the course of lectures delivered by the author for many years at the Lomonosov Moscow State University. The author thanks his colleagues at the Moscow University, as well as at other universities and institutes, for helpful discussions without which it would have been impossible to give the book its present form. The author is also grateful to Acad. M.A. El'yashevich of the Belorussian Academy of Sciences and the staff of the General Physics Department of the Ural State University headed by Prof. L. Ya. Kobelev for a careful review of the manuscript and valuable suggestions.

A. N. Matveev

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Statistical Method

Starting point: The dynamic description of a many-particle system is technically unrealizable, theoretically unsuitable, and practically useless.

Basic idea: A many-particle system is characterized by statistical parameters and laws.

Mathematical apparatus: Theory of random processes and quantities.

Sec. 1. METHODS OF INVESTIGATING MANY-PARTICLE SYSTEMS

The properties of the states of aggregation of matter are considered and the models of many-particle systems are described.

It is revealed that the dynamic description of many-particle systems is not suitable from ■ theoretical point of view, not feasible from ■ technical point of view, and not useful from ■ practical point of view.

The main features of the statistical and thermodynamic methods are described.

LIMITS OF APPLICABILITY OF THE MATERIAL POINT MODEL AND THE PERFECTLY RIGID BODY MODEL. Mechanics deals with the motion of material bodies whose properties can be modelled by using the concepts of ■ material point and ■ perfectly rigid body. This means that in the first case, the internal structure and size of the material body are not taken into account, while in the second case, these properties are considered only to investigate the distribution of the inertial property (density) over the volume occupied by the material body for the special case when this distribution is invariable in time. Thus, the internal properties and internal motions of material bodies are not taken into account in the second case also. The density distribution is assumed to be given for the motion of a perfectly rigid body as ■ whole. Hence, the models of a material point and a perfectly rigid body are inapplicable for investigating the internal properties of material bodies when their structure and the relative motion of the parts of the bodies are significant.

THE MATERIAL BODY MODEL. It is known that material bodies consist of atoms and molecules whose structure is also known. Hence, the model of a material body is the aggregate of atoms and molecules which interact and move according to certain laws. In turn, the atoms and molecules constituting ■ material body may be represented by different models

depending on the circumstances and the nature of the phenomena being considered. In some cases, the atoms and molecules can be considered as material points, in other cases they are treated as perfectly rigid material bodies, while sometimes their internal structure and motion have to be taken into consideration. Since the structure of atoms and molecules can be fully investigated by the quantum-mechanical methods, all their properties are assumed to be known. Consequently, the properties of the models used for representing them in specific cases are also assumed to be known.

In principle, the interaction of atoms and molecules and their motion are also known. In some cases this motion is considered purely classically by the same methods which are used for investigating the motion of material points and rigid bodies, while in some other cases, it is necessary to consider quantum-mechanical laws which characterize the motion of microparticles. These laws are known from quantum mechanics. Their content is not so important here. It is important just to state that these laws are known and can be used in principle for investigating the interaction and the motion of atoms and molecules constituting material bodies.

Hence, a material body can be modelled as an aggregate of atoms and molecules whose properties, laws of motion, and interactions are known.

ATOMIC AND MOLECULAR MASS. In molecular physics, the mass of atoms and molecules is characterized not by its absolute value (in kilograms), but by relative dimensionless quantities called the relative atomic mass A_r and the relative molecular mass M_r .

For the atomic mass unit m_u , $1/12$ of the mass of ^{12}C isotope of carbon is taken:

$$m_u = \frac{\text{mass of } ^{12}\text{C isotope}}{12} = 1.66 \times 10^{-27} \text{ kg.} \quad (1.1)$$

The relative molecular mass, or the relative mass of a molecule, is defined by the formula

$$M_r = \frac{m_{\text{mol}}}{m_u} = \frac{\text{molecular mass}}{\text{mass of } ^{12}\text{C}} \times 12 \text{ (dimensionless),} \quad (1.2)$$

where m_{mol} is the absolute value of the molecular mass in kilograms. The relative atomic mass is also defined by a similar formula, but in this case m_{mol} in (1.2) denotes the absolute atomic mass.

In order of magnitude, the absolute values of atomic mass approximately lie in the interval 10^{-25} - 10^{-27} kg, while the

relative atomic masses range from 1 to 10^2 . The relative molecular masses are distributed over a much wider interval from unity to several hundreds of thousands (see Sec. 49).

AMOUNT OF SUBSTANCE. In SI units, the amount of substance is characterized by the number of its structural elements, and is expressed in moles. A mole is equal to the amount of substance of a system in which the number of structural elements is the same as the number of structural elements (atoms) in 0.012 kg of ^{12}C isotope of carbon. Thus, a mole of any substance contains, by definition, the same number of atoms, called the **Avogadro number**. It is equal to

$$N_A = \frac{0.012 \text{ kg}}{12m_u} \text{ mole}^{-1} = \frac{10^{-3} \text{ kg}}{m_u} \text{ mole}^{-1} \\ = 6.02 \times 10^{23} \text{ mole}^{-1}, \quad (1.3)$$

where m_u is defined by (1.1). It follows from (1.3) that

$$m_u N_A = 10^{-3} \text{ kg/mole}. \quad (1.4)$$

The concept of a mole reflects the number of structural elements in a substance. Hence, these elements must always be indicated, otherwise the definition of the amount of substance in moles loses its meaning. For example, it is incorrect to say that a vessel contains two moles of water. The correct way to put it will be "the vessel contains two moles of water molecules". This means that the vessel contains $2 \times 6.02 \times 10^{23}$ molecules of water. If, for example, 10^{24} free electrons are contained in a certain volume, it can be stated that this volume contains $10^{24}/(6.02 \times 10^{23}) = 1.66$ mole of electrons. Or, if a certain quantity of water contains, for instance, one mole of water molecules, it will contain two moles of hydrogen atoms and one mole of oxygen atoms, or 10 moles of protons, 8 moles of neutrons, and 10 moles of electrons (heavy water molecules and isotopes are not taken into consideration).

In molecular physics, the concept of molar mass is also used. It is defined as the mass of one mole of the substance:

$$M = m_{\text{mol}} N_A, \quad (1.5)$$

where m_{mol} is the molecular mass. The molar mass is expressed in kilograms per mole (kg/mole). Taking into account Eqs. (1.2) and (1.4), we can express formula (1.5) in the following form:

$$M = m_{\text{mol}} \times 10^{-3}/m_u = 10^{-3} M_r \text{ kg/mole}, \quad (1.6)$$

where M_r is the dimensionless relative mass defined by (1.2).

In particular, the molar mass of a substance consisting of ^{12}C carbon isotopes is equal to 12×10^{-3} kg/mole. The relative atomic masses are given in the Mendeleev Periodic Table. The relative molecular masses can be determined, with a sufficiently high degree of accuracy, as the sum of relative masses of atoms constituting the molecule, since the energy of the chemical bond of atoms in a molecule and the mass defect corresponding to this bond are small.

The number ν of moles of a certain amount of substance is connected with the number n of its structural elements (molecules) through the relation

$$\nu = n/N_A. \quad (1.7)$$

Multiplying the numerator and denominator of the right-hand side of this equation by the mass of a molecule, considering that the mass of a substance is defined as $m = m_{\text{mol}} n$, and taking into account Eq. (1.5), we obtain

$$\nu = m/M. \quad (1.8)$$

STATES OF AGGREGATION OF A SUBSTANCE. An investigation of interaction between atoms and molecules shows that forces of attraction come into play at relatively large distances, while repulsive forces prevail at small distances. These forces are electromagnetic in origin. The existence of repulsive forces at small distances merely states the fact that atoms and molecules occupy a certain volume in space, thereby obstructing other atoms and molecules from occupying the same volume.

Atoms and molecules are in perpetual motion and hence possess a certain kinetic energy. Obviously, the forces of attraction tend to combine atoms and molecules into a single entity, while the kinetic energy of molecules and atoms hinders this tendency of adhesion between them. The final result of the competition between these two tendencies depends on their relative intensity. If the tendency to separate is stronger than the tendency to unite, the substance is in the gaseous state. If, on the other hand, the tendency to unite is stronger, the substance is in the solid state. When these two tendencies are of nearly the same intensity, the liquid state is formed. All these remarks are qualitative since no quantitative measures for "intensity" have been given. Such quantitative measures are the potential energy of attraction and the kinetic energy. If the total kinetic energy of atoms and molecules is much higher than the total potential energy of their mutual attraction (in absolute value since the potential energy of attraction is negative), the substance is in

! The state of aggregation of a substance is determined by the relation between the average kinetic energy and the average potential energy of interaction between molecules: the average kinetic energy of gases is much higher than the average potential energy of interaction between molecules; in liquids these values are nearly equal, while in solids the absolute value of the average potential energy of molecular interaction is much higher than the average kinetic energy. (It should be recalled that the potential energy of interaction is negative in the case of attraction.)



Mikhail Vasil'evich
Lomonosov
(1711-1765)

the gaseous state. In the opposite case, the substance is a solid. The liquid state indicates that these energies are nearly equal.

The molecular kinetic theory of structure of matter explains the properties of substances on the basis of their molecular structure, motion, and intermolecular interaction. This theory was developed over several hundreds of years, and a significant contribution towards this was made by M.V. Lomonosov.

BASIC FEATURES OF THE STATES OF AGGREGATION.

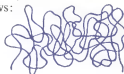
Since the gaseous state is formed as a result of a complete suppression of the adhesive tendency of molecules, a substance in the gaseous state retains neither its shape nor its volume. Its volume and shape are determined by the vessel in which it is contained. If there is no vessel to contain a gas, it tends to fill the entire space. The molecular motion in gases proceeds as follows: each molecule moves without interaction for most of the time, changing its direction in a small region as a result of collision with another molecule. The distance covered by a molecule between collisions is hundreds and thousands of times larger than its diameter. A simultaneous collision of three or more molecules is a rare event. The trajectory of an individual molecule looks as follows:



The molecules and atoms in a solid are tightly bound with one another. A substance in the solid state retains its shape as well as volume. A deformation (change in the shape or volume) induces forces which tend to restore both the shape and the volume. Molecules or atoms in a solid occupy specific positions and form a crystal lattice. They vibrate about certain mean positions called the lattice sites of the crystal. As a rule, they cannot leave a certain region near the lattice sites. The line along which vibrations take place and the amplitude of vibrations change with time, but these changes occur over a period longer than the period of vibrations. Quite a large number of vibrations occur along a fixed line before its direction changes. Taking this into account, the trajectory of an individual molecule can be represented as a sequence of linear vibrations of different amplitudes and in different directions:



In the liquid state, a substance tends to retain its volume, but not its shape. It should be noted that the spherical shape of liquids under zero gravity does not contradict this statement. A liquid always assumes the shape determined by the forces acting on it. Under zero gravity, only the forces of surface tension act on it, and the spherical shape corresponds to the general equilibrium condition. Molecules in a liquid are close to each other, being as if in contact. Their relative positions, however, are not fixed and vary rather slowly. The trajectory of a molecule is schematically represented as follows:



Sometimes, a large number of molecules combine to form an aggregate, and their distribution within the aggregate is ordered in a certain way. In this case, liquids have some properties typical of solid crystals, and are called liquid crystals. At present, the theories of gaseous and solid states are quite satisfactory. The theory of liquid state is the one least developed.

THE IDEAL GAS MODEL. The simplest model of many-particle system is an ideal gas. By definition, this is a gas of point particles with a finite mass, which are characterized by the absence of long-range forces and by elastic collisions. It should be emphasized that the particles collide with one another only according to such a mechanism since, strictly speaking, point particles undergo only head-on collisions, which reverse the direction of velocities of the colliding particles, and do not change their velocities by any other angle. The closest approximation to an ideal gas is a highly rarefied gas.

The simplicity of the ideal gas model makes it suitable for investigating many-particle systems and related concepts.

THE DYNAMIC METHOD. Between collisions, particles move in straight lines. The laws of collisions and impacts against the walls of the vessel in which a gas is contained are known. Hence, knowing the positions and velocities of all the gas particles at a certain instant of time, we can calculate their positions and velocities at all subsequent moments of time. Moreover, in principle, we can also find the positions and velocities of all the particles at all preceding moments of time if necessary. The positions and velocities of all particles at any instant of time give the most detailed information

! Ideal gas exists only in theory, and simply cannot exist in reality: the assumption that the molecules are noninteracting point particles is equivalent to the admission of their existence outside the space, i.e. of their nonexistence.

The dynamic description of a many-particle system is technically unrealizable, theoretically unsuitable, and practically useless.

The statistical and thermodynamic methods of investigating many-particle systems supplement each other.

about a system of particles. However, all this information in its direct form is mentally incomprehensible, and the simplest interpretation is beyond any technical means, let alone the fact that its processing is unrealizable technically.

Indeed, 1 cm^3 of air under normal conditions contains $\sim 2.7 \times 10^{19}$ molecules. This means that $6 \times 2.7 \times 10^{19}$ numbers have to be fixed in order to describe the positions and velocities of all molecules at a certain instant of time. If some instrument could fix these numbers at the rate of 1 million per second, it would take $6 \times 2.7 \times 10^{13} \text{ s} \approx 6$ million years. If these data are used for calculating, for example, the kinetic energy of particles at a rate of 10^6 operations per second, it would take about 21 million years, even if we do not take into account the 2 million years required to fix the kinetic energy values for all molecules. On top of this, all this information corresponds to a certain instant of time for molecules contained in 1 cm^3 of air under normal conditions. Naturally, such a problem is technically unrealizable.

However, it is not just this circumstance that makes the dynamic consideration impossible and impractical. As a matter of fact, the information about the individual particles in its direct form is unsuitable for theoretical analysis. For example, 10^9 molecules in this volume numerically mean less than one person in the universe. Hence, if we had detailed information about all the people living in this world, the loss of information about one person would be more important than the loss of information about 10^9 molecules in the system under consideration. Naturally, such a volume of information in itself is not important for investigating a system of particles as a whole. This is important for estimating the role of bits of information obtained from a dynamic description. A direct consequence of this circumstance is even more important. Suppose that the directions of velocities of 10^9 molecules are changed. Obviously, these changes are as insignificant for the system of particles on the whole as an acute toothache of a human being for the humanity at large. However, insignificant changes within a fraction of a second will lead to a complete alteration of the positions and velocities of all the particles, and consequently, to a complete alteration of the entire information in the form under consideration. This is due to the fact that each molecule undergoes about 10^9 collisions per second under normal circumstances. Therefore, if the velocity of one of the molecules slightly changes its direction, the velocities of 2^n molecules will change in $n \times 10^{-9} \text{ s}$. Consequently, their positions in space will change in

comparison with the positions which would be occupied by the molecules if the velocity of the initial molecule were unchanged. This means that a slight variation, for example, in the direction of the velocity of one molecule will soon lead to a variation of the velocity and position of all the molecules. This shows that such a form of information is unsuitable for a theoretical analysis of the behaviour of the system as a whole and is useless from a practical point of view.

On the basis of the above discussion, it can be concluded that a dynamic description of a many-particle system is technically unrealizable, theoretically inapplicable, and practically useless.

THE STATISTICAL METHOD. The above dynamic description immediately leads to the conclusion that for the investigation of a many-particle system, the information must be of a general nature, pertaining to an aggregate of a large number of particles rather than to individual particles. Accordingly, the concepts must also refer to aggregates of particles. A different approach must be adopted for the new type of information and new concepts. This approach is called the statistical method. The laws describing the behaviour of aggregates of a large number of particles, which are analyzed by the statistical method, are called statistical laws. Statistical methods are used more widely in physics than dynamic methods. This is due to the fact that a dynamic method can be effectively applied only to systems with a small number of degrees of freedom. Most physical systems, however, have an enormous number of degrees of freedom and can be investigated only with the help of statistical methods. Besides, the quantum-mechanical laws are also statistical in nature. Consequently, it is necessary to use statistical methods even for the analysis of systems with a small number of degrees of freedom if quantum-mechanical effects are significant in their behaviour. All this points towards the tremendous role of statistical methods and statistical laws in physics.

THE THERMODYNAMIC METHOD. A many-particle system can be investigated in a different way without going into details of its internal structure. In such an approach, we must use the concepts and physical quantities pertaining to the system as a whole. For example, the model of an ideal gas in the state of equilibrium in this case is characterized by the volume, pressure, and temperature. The relations between these quantities must be established experimentally, and the theory must be based on some general postulates (for example, the law of conservation of energy) explaining these relations. Such a theory is phenomenological in nature, and

?

1. What are the main features of the model of a substance in molecular physics?
2. What are the main criteria of different states of aggregation of a substance?
3. Why is the dynamic description of a many-particle system technically unrealizable, theoretically inapplicable, and practically useless?
4. Outline the main features of the thermodynamic method for describing a many-particle system.

does not deal with internal mechanisms of processes determining the behaviour of the system as a whole. Such a method of investigating many-particle systems is called **thermodynamic**.

Statistical and thermodynamic methods of investigating many-particle systems are complementary to each other. The thermodynamic method is of a general nature and can be used for studying phenomena without knowing their internal mechanisms. The statistical method helps to understand the essence of phenomena and establish a relation between the behaviour of a system as a whole and the behaviour and properties of individual particles and subsystems. A combined application of these methods helps in solving scientific problems in the most effective way.

Example 1.1. Find the molar mass of water. How many moles of water molecules are contained in 1 kg of water? How many molecules of water are contained in 1 g? What is the mass of a water molecule?

The relative mass M_r of a water molecule is 18. Hence, the molar mass of water is $M = 18 \times 10^{-3}$ kg/mole. The number of moles ν in 1 kg of water is equal to $1 \text{ kg} / (18 \times 10^{-3} \text{ kg/mole}) = 10^3 / 18 = 55.6$ moles. The mass of a water molecule $m_{\text{mol}} = M_r m_u = 18 \times 1.66 \times 10^{-27} \text{ kg} = 2.99 \times 10^{-26} \text{ kg}$. The number of molecules in 1 g = 10^{-3} kg is $n = m / m_{\text{mol}} = 10^{-3} / (2.99 \times 10^{-26}) = 3.33 \times 10^{22}$.

Alternatively, the number of molecules in 1 g of water can be found with the help of the Avogadro number. The number of moles contained in 10^{-3} kg of water is $\nu = [10^{-3} / (18 \times 10^{-3})] = 0.056$ mole. Consequently, the number of molecules $n = \nu N_A = 0.056 \times 6.02 \times 10^{23} = 3.33 \times 10^{22}$.

Example 1.2. It is known that the volume occupied by a water molecule is $\Delta V \approx 3 \times 10^{-29} \text{ m}^3$. Find the density of water.

Since the mass of a water molecule $m_{\text{mol}} = 2.99 \times 10^{-26} \text{ kg}$, its density $\rho = m_{\text{mol}} / \Delta V = 10^3 \text{ kg/m}^3$ (we can assume that the molecules are densely packed).

Sec. 2. MATHEMATICAL CONCEPTS

The basic concepts of the probability theory and methods of studying random phenomena are considered. The main properties of random quantities are analyzed.

STATEMENT OF THE PROBLEM. It was shown in Sec. 1 that while the information about the positions and velocities of all individual particles of an ideal gas is conceivably the most comprehensive information, it is inapplicable for analyzing the properties and behaviour of a system in its direct form. In order to use the data contained in this information, it should be reduced to certain generalized characteristics of the aggregates of particles in such a way as to reflect the most significant properties of these aggregates and to make their concepts and mathematical formulation easier. These questions are considered by the probability theory and mathematical statistics. Large mathematical treatises are devoted to these problems. In this book, only the most essential mathematical results are given. The physical meaning of the mathematical concepts is mainly illustrated by considering the example of an ideal gas. Readers interested in details of the mathematical treatment are referred to appropriate courses.

RANDOM EVENTS. The rejection of the dynamic description of a many-particle system alters the statement of the problem of describing such systems. If we isolate a certain small region in the space occupied by an ideal gas, we cannot specify the time when an individual particle will be located inside this region in the course of its motion. Similarly, it cannot be indicated whether this particle will stay in the region under consideration for a specific time interval. Hence, the location of a particle in a certain region of space is a random event.

The random nature of some phenomena is subjective and is due to an insufficient knowledge or lack of technical facilities for their exact prediction. More frequently, however, the random nature of events is objective in principle and the very question of the exact prediction of events is devoid of any physical meaning.

For example, let us consider an "event" involving a "collision" of a man with an automobile in a certain region of space, i.e. in a certain street. This collision is a consequence of a certain sequence of events culminating in the arrival of the automobile at the site of accident at an appropriate moment of time. Another chain of events is linked with the man and culminates in his arrival at the site of accident at the same instant of time. The chains of events associated with the automobile and the man are not connected physically, i.e. a variation in the chain of events associated with the automobile does not cause any variation

in the chain of events associated with the man. Hence, in principle, it is impossible to exactly predict the running over of a man by an automobile. Such a formulation of the problem has no physical sense by the very nature of the events under consideration. Such an event is random in the objective sense and not because we lack the knowledge or the technical facilities to predict this event.

The motion of microparticles is described by the laws of quantum mechanics. It is impossible in principle to predict their exact location. Hence, the position of a microparticle in a certain region of space is a random event by nature and not because of insufficient knowledge or lack of technical facilities for its prediction. This confirms the above statement that most of the events in a many-particle system are random.

In order to describe random events, we must use special concepts and appropriate mathematical methods. The probability theory deals with such problems.

RANDOM QUANTITIES. The coordinates and velocities of individual molecules in an ideal gas at a certain instant of time cannot be taken as numbers whose exact values can be predicted beforehand. These are random quantities. The theory of probability and mathematical statistics deals with the laws describing the behaviour of random quantities.

PROBABILITY. A huge variety of random events is analyzed in theory and practice. The general result of such an analysis, however, is always formulated in the same way: either the event has occurred or it has not occurred. The problem of predicting random events is reduced to finding the quantitative characteristics of these "either... or" possibilities and is solved with the help of the probability concept.

THE DEFINITION OF PROBABILITY IN TERMS OF FREQUENCY. Let us divide the volume occupied by an ideal gas into two equal parts. We shall assume that we can distinguish the particles from one another and can track the position of an individual particle without significantly influencing the motion of the particle and the state of the system as a whole through the act of observation. Suppose that the external conditions of the system are invariable. Let us consider an event consisting in that the particle under consideration is in a particular half of the volume. Then the result of each observation is reduced to the statement that the event has either occurred, i.e. the particle is located in the particular half, or that the event has not occurred, i.e. this half does not contain the particle. We use the following notation: N is the total number of observations or "trials",

N_A is the number of trials in which the event occurs, i.e. the particle is located in the particular half, and A is the event itself. The probability of occurrence of the event A is given by the formula

$$\mathcal{P}(A) = \lim_{N \rightarrow \infty} \frac{N_A}{N}. \quad (2.1)$$

Here, it is important that the number of trials in a system under invariable conditions be very large ($N \rightarrow \infty$). Instead of requiring that the trials be made on the same system under invariable conditions, we can consider a set of separate trials on a large number of identical systems, called an ensemble of systems. Hence, the number N_A in formula (2.1) is the number of systems in an ensemble, corresponding to the location of a particle in the given half of the volume, and N is the total number of systems in the ensemble. Naturally, these definitions are exactly equivalent, although one of them may turn out to be more convenient for the theoretical calculation of probabilities under certain conditions.

If we make a sufficiently large number of trials, the calculation of probability with the help of formula (2.1) is a simple mathematical operation. However, it is very difficult to calculate the probability of a certain event with the help of this formula, since we cannot predict the number of trials N_A in which this event will occur. But this is exactly the form to which the problem is reduced when analyzing any processes of probabilistic nature. The combination theory is frequently helpful in analyzing such problems. It can be used for calculating the factors favouring the occurrence of a certain event among many. The intuitive concept of equally probable events is the starting point for such an analysis, and its mathematical expression merely states that the frequency of their occurrence is the same. This sometimes helps in calculating the number N_A in formula (2.1) and thus determining the probability. This method will be repeatedly used in this book. But first let us illustrate it by considering some simple examples.

If a particle moves in a volume mentally divided into two equal parts, there are no physical grounds to assume that the particle will be located in one of the halves in preference to the other. Hence, the probability of the particle occupying either half of the volume is the same, and the particle can be found in either half with the same probability in each observation or trial. Consequently, for a large number of observations, the particle will be found in half of the cases in



It is meaningless to ask why a particular event occurs out of two equally probable events in a given experiment. Such a problem was discussed in the Middle Ages. Two exactly identical stacks of hay are placed symmetrically in front of an ass (Buridan's ass) so that there are no motives for him to prefer one stack to the other. What will happen to the ass? According to one opinion, the ass would starve to death. Such a logic does not satisfy the ass. It does not satisfy the scientists either.

one part of the volume and in half of the cases in the other part, which means that $N_A = N/2$ and $\mathcal{P}(A) = 1/2$. Similar arguments apply to the tossing of a coin for "heads", casting dice, etc. In all cases, the problem boils down to the calculation of equally possible outcomes of the trials. Therefore, the calculation of probability by formula (2.1) with the help of the combination theory methods is carried out as follows: if a trial can lead to N equally probable results, and if the event A occurred N_A times out of these, its probability is given by formula (2.1). For example, if we cast dice with six faces having numbers 1, 2, 3, 4, 5, and 6 engraved on them, equally possible outcomes of N casts of a die is the appearance of any of these numbers on the upper face. For example, the number 1 appears on top in $N/6$ outcomes. Consequently, $N_1 = N/6$ for this event, and its probability $\mathcal{P}(1) = 1/6$. The probabilities of appearance of "two", "three", etc. are calculated in a similar way:

$$\mathcal{P}(1) = \mathcal{P}(2) = \dots = \mathcal{P}(6) = 1/6.$$

It should be noted that an individual die is a statistical system, while a set of N identical dice constitutes an ensemble.

PROBABILITY DENSITY. If an event is characterized by continuously varying quantities, there is no sense in calculating the probability with the help of formula (2.1). For example, it is meaningless to ask "what is the probability that a particle has a velocity of 10 m/s?" This is due to the fact that "the number" of all possible velocities cannot be counted, since the velocity is a continuous quantity. The set of events in this case is uncountable, and their probabilistic description is carried out by using the concept of probability density.

Imagine a closed vessel with a gas under invariable external conditions. The gas molecules move randomly in the vessel, although it certainly does not mean that all parts of the vessel volume are equivalent for them. For example, if the vessel is in a gravitational field, the lower part of the vessel is preferable for the molecules as compared to the upper part, although the molecules can be found in all parts of the vessel. Suppose that we can somehow determine the location of a certain isolated molecule without perturbing its motion or altering its location through the act of measurement. In different observations the molecule will be found at different points. We divide the entire space, including that outside the vessel, into small volume elements ΔV_i . Obviously, the number of such regions is infinite ($i = 1, 2, \dots$). The number of acts of observations is denoted by N . In each act, the

molecule is found in a certain volume ΔV_i . Suppose that the molecule is found N_i times in the volume ΔV_i in N acts of observation ($N \rightarrow \infty$). Then, in accordance with the definition (2.1), the probability of the molecule being found in the volume ΔV_i in the next act of observation will be

$$\mathcal{P}(\Delta V_i) = \lim_{N \rightarrow \infty} \frac{N_i}{N}.$$

If we are dealing with a closed vessel, the molecule is never observed in all the regions ΔV_i outside the vessel. In other words, $N_i = 0$ for these regions, and the probability of the molecule being found in the regions outside the vessel will be $\mathcal{P}(\Delta V_i) = 0$.

Inside the vessel, this probability is generally nonzero and is not constant even for equal volumes ΔV_i . For example, if the vessel is in a gravitational field, the probability near the bottom of the vessel will be somewhat higher than at the top. However, this probability depends on the volume ΔV_i and is therefore not suitable as a basic concept. Therefore, we use the concept of probability density defined by the formula

$$f(x, y, z) = \lim_{\Delta V_i \rightarrow 0} \frac{\mathcal{P}(\Delta V_i)}{\Delta V_i} = \lim_{\substack{\Delta V_i \rightarrow 0 \\ N \rightarrow \infty}} \frac{N_i}{\Delta V_i N}, \quad (2.2a)$$

where x , y , and z are the coordinates of the point to which an infinitely small volume ΔV_i contracts. Thus, the probability density is the probability of finding a molecule in an infinitely small volume divided by this volume. In other words, it is defined like any other density, for example the mass density $\rho = \lim_{\Delta V \rightarrow 0} (\Delta m / \Delta V)$. In the same way as (2.2a), we

can define the probability density on a two-dimensional manifold (surface), one-dimensional manifold, or a multidimensional manifold with more than three dimensions.

It follows from (2.2a) that if N_0 observations are made, the molecule will be found in the volume dV in the neighbourhood of the point (x, y, z) in

$$dN = N_0 f(x, y, z) dV = N_0 f(x, y, z) dx dy dz$$

cases. In a finite volume V_1 , the molecule will be observed $N(V_1) = N_0 \int_{V_1} f(x, y, z) dx dy dz$

times. It follows hence that the probability $\mathcal{P}(V_1)$ of

a molecule being found as a result of observation in the volume V_1 will be

$$\mathcal{P}(V_1) = \frac{N(V_1)}{N_0} = \frac{1}{V_1} \int_{V_1} f(x, y, z) dx dy dz$$

Thus, if we know the probability density, we can find the probability for any region in which the density is defined. For a gas in a closed vessel, the probability density at the points outside the vessel is equal to zero.

If the entire space $V_1 \rightarrow \infty$ is taken as the volume V_1 , a particle will be found at some point of the space in each trial, and hence the number of observations of the particle in the volume $V_1 \rightarrow \infty$ is equal to the number of trials N_0 , i.e. $N(V_1 \rightarrow \infty) = N_0$. The probability of finding the particle in the volume $V_1 \rightarrow \infty$ (i.e. at any point of the space) is

$$\mathcal{P}(V_1 \rightarrow \infty) = \frac{N(V_1 \rightarrow \infty)}{N_0} = 1 = \int_{V_1 \rightarrow \infty} f(x, y, z) dx dy dz.$$

The condition

$$\int_{V_1 \rightarrow \infty} f(x, y, z) dx dy dz = 1 \quad (2.2b)$$

is called the probability density normalization condition. It shows that the molecule will be found at some point of the space in every act of observation. In other words, it expresses the fact of existence of the molecule.

If it is known that a molecule is in a closed volume V confined by the vessel walls, the normalization condition assumes the form

$$\int_V f dV = 1.$$

Suppose that there are no grounds to assume that different regions inside the vessel are not equivalent for the molecules. For example, the vessel is in an inertial system of coordinates (i.e. there is no gravitational field) at a certain temperature. In this case, obviously, the probability density has a constant value: $f_0 = \text{const}$. Its value can be found from the normalization condition

$$\int_V f_0 dV = f_0 \int_V dV = f_0 V = 1.$$

Consequently, the probability density in this case will be $f_0 = 1/V$.



The admission of the random nature of events does not mean that there is no causal interaction between them.

The causal interaction between events is universal, while the nature of determinism may be different. For example, the determinism may be only statistical.

The random nature of the events does not mean that they cannot be regulated or controlled. In order to increase the chances of winning a lottery, one should buy more tickets. The possibility of influencing random events was expressed long ago in the saying: "Trust in God and do the right".

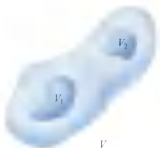


Fig. 1. Continual interpretation of probabilities

Next, if the volume V_1 is a part of the volume V , the molecule will be found

$$N(V_1) = N_0 \int_{V_1} f_0 dV = N_0 \frac{1}{V} \int_{V_1} dV = N_0 \frac{V_1}{V}$$

times in this volume during N_0 observations. Hence, the probability of finding the molecule in the volume V_1 will be

$$\mathcal{P}(V_1) = [N(V_1)/N_0] = V_1/V. \quad (2.2c)$$

This formula is valid only for a constant probability density in the volume V and if it is known that the molecule is sure to be found in this volume. However, for the sake of clarity, it can be used for illustrating the general theorems of the probability theory. A rigorous proof of the theorems can be carried out on the basis of the general definition (2.1) of probability.

SUMMATION OF THE PROBABILITIES OF MUTUALLY EXCLUSIVE EVENTS. Suppose that we have two mutually exclusive events. For example, if there are two nonoverlapping regions V_1 and V_2 (Fig. 1) in a volume V , the presence of a particle in the region V_1 rules out the possibility of this particle being found in the region V_2 . Consequently, the detection of the particle in the volume V_1 and its presence in the volume V_2 are two mutually exclusive events.

Let us consider the event when the particle is either in the volume V_1 or in the volume V_2 . The probability of this event

$$\mathcal{P}(V_1 + V_2) = \frac{V_1 + V_2}{V} = \frac{V_1}{V} + \frac{V_2}{V} = \mathcal{P}(V_1) + \mathcal{P}(V_2) \quad (2.3)$$

is the sum of the probabilities of finding the particle in the volumes V_1 and V_2 . Formula (2.3) represents the probability summation rule for two mutually exclusive events.

Let us apply this rule to the casting of dice. The appearance of the numbers 1, 2, ... on the upper face are mutually exclusive events. Hence, the probability that either 1 or 2 appear on the upper face is equal to

$$\mathcal{P}(1 + 2) = \mathcal{P}(1) + \mathcal{P}(2).$$

Thus, the general formula for probability summation of two mutually exclusive events A and B has the form

$$\mathcal{P}(A + B) = \mathcal{P}(A) + \mathcal{P}(B), \quad (2.4)$$

where $\mathcal{P}(A + B)$ is the probability of the occurrence of either event A or event B . The simultaneous occurrence of these two events is ruled out, while it is possible that neither of the events occurs at a certain time.

NORMALIZATION OF PROBABILITY. Suppose that all equally possible outcomes of trials are known for a given system and that they comprise a certain number of different mutually exclusive events (cases) which can be assigned the indices 1, 2, ..., n for the sake of convenience. We denote by N_i the number of outcomes of trials in which the event denoted by the index i is realized. Accordingly, we can write

$$N_1 + N_2 + \dots + N_n = \sum_{i=1}^n N_i = N. \quad (2.5)$$

This gives

$$\sum_{i=1}^n \frac{N_i}{N} = \sum_{i=1}^n \mathcal{P}_i = 1,$$

where $\mathcal{P}_i = N_i/N$ is the probability of the i th event. The formula

$$\sum_{i=1}^n \mathcal{P}_i = 1 \quad (2.6)$$

is called the **normalization condition for probabilities**. According to this condition, the set of mutually exclusive events under consideration is complete, i.e. each outcome of trials belongs to this set.

SUMMATION OF PROBABILITIES IN THE GENERAL CASE. If a simultaneous occurrence of the events A and B is not ruled out, formula (2.4) for the summation of probabilities must be altered. Suppose that N is the total number of trials. The events A and B occurred in N_A and N_B outcomes of these trials respectively. All the remaining outcomes involved neither of the two events A and B . However, the cases N_A and N_B also include the cases when the events A and B occur simultaneously. We shall denote the number of such events by N_{AB} . These outcomes were taken into account twice: once with the event A and once with the event B . Therefore, the total number of events A or B is equal to

$$N_{A+B} = N_A + N_B - N_{AB}.$$

Dividing both sides of this equation by N , we get

$$\sum_{i=1}^n \mathcal{P}_i = 1$$



Fig. 2. To probability summation and conditional probability

$$\mathcal{P}(A + B) = \mathcal{P}(A) + \mathcal{P}(B) - \mathcal{P}(AB), \quad (2.7)$$

where

$$\mathcal{P}(AB) = N_{AB}/N \quad (2.8)$$

is the probability of simultaneous occurrence of the events A and B . If it is equal to zero, i.e. if the events are mutually exclusive, formula (2.7) is reduced to formula (2.4).

Formula (2.7) assumes an especially clear visual form if we turn to the continuum interpretation of the probability [see (2.2c)]. Suppose that the regions V_1 and V_2 overlap (Fig. 2). We denote the region of their intersection by V_{12} . The volume of the region obtained as a result of summation of V_1 and V_2 will be equal to $V_1 + V_2 - V_{12}$. Consequently, the probability of a particle being found in this volume is

$$\begin{aligned} \mathcal{P}(V_1 + V_2) &= \frac{V_1 + V_2 - V_{12}}{V} \\ &= \frac{V_1}{V} + \frac{V_2}{V} - \frac{V_{12}}{V} = \mathcal{P}(V_1) + \mathcal{P}(V_2) - \mathcal{P}(V_{12}), \end{aligned}$$

where $\mathcal{P}(V_{12}) = V_{12}/V$ is the probability of finding the particle in the region of intersection of V_1 and V_2 .

CONDITIONAL PROBABILITY. The probability of occurrence of any event A under the condition that an event B has occurred is called the **conditional probability** of the occurrence of the event A and is denoted by $\mathcal{P}(A/B)$.

Since the total number of outcomes of trials in which the event B occurs is equal to N_B , out of which the event A also occurs N_{AB} times, we can write

$$\mathcal{P}(A/B) = N_{AB}/N_B. \quad (2.9)$$

In the continuum definition of probability, the conditional probability $\mathcal{P}(V_1/V_2)$ of finding a particle in the volume V_1 if it is contained in the volume V_2 is reduced to calculating the probability of finding the particle in the volume V_{12} if it is contained in the volume V_2 . Hence,

$$\mathcal{P}(V_1/V_2) = V_{12}/V_2.$$

It is convenient to transform formula (2.9) by dividing the numerator and the denominator of the right-hand side by N :

$$\mathcal{P}(A/B) = \frac{N_{AB}/N}{N_B/N} = \frac{\mathcal{P}(AB)}{\mathcal{P}(B)}, \quad (2.10)$$

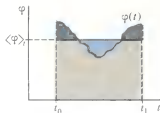


Fig. 3. Geometrical meaning of the mean value: the area under the straight line $\langle \varphi \rangle$, between t_0 and t_1 is equal to the area under the curve $\varphi(t)$

where $\mathcal{P}(AB)$ is the probability of simultaneous occurrence of events A and B , which is defined by (2.8).

The expression (2.10) in the form

$$\mathcal{P}(AB) = \mathcal{P}(B)\mathcal{P}(A/B) = \mathcal{P}(A)\mathcal{P}(B/A) \quad (2.11)$$

is called the **probability multiplication rule**.

INDEPENDENT EVENTS. If the probability of occurrence of any event is independent of the occurrence of another event, such events are called **independent**. This means that if, for example, the event A is independent of the event B , $\mathcal{P}(A/B) = \mathcal{P}(A)$. For independent events, formula (2.11) assumes the form

$$\mathcal{P}(AB) = \mathcal{P}(A)\mathcal{P}(B). \quad (2.12)$$

It is often applied for calculating the probability of simultaneous occurrence of independent events, as well as for verifying the independence of the events under investigation.

Probability multiplication rule for many events is obtained directly from the formula (2.11). For example, the probability of simultaneous occurrence of events A , B , and C is defined by

$$\mathcal{P}(ABC) = \mathcal{P}(AB)\mathcal{P}(C/AB) = \mathcal{P}(A)\mathcal{P}(B/A)\mathcal{P}(C/AB). \quad (2.13)$$

For independent events, we have

$$\mathcal{P}(ABC) = \mathcal{P}(A)\mathcal{P}(B)\mathcal{P}(C). \quad (2.14)$$

This formula expresses the **necessary and sufficient condition of independence of three events**.

MEAN VALUE OF A DISCRETE RANDOM QUANTITY. If a random quantity X assumes a number of values $x_1, x_2, \dots, x_N$, its mean value will be defined as

$$\langle x \rangle = \frac{1}{N} \sum_{i=1}^N x_i. \quad (2.15)$$

Some of the values x_i can be identical, hence the sum over i on the right-hand side of (2.15) must be regrouped in such a way as to contain only different values x_j :

$$\langle x \rangle = \sum_j (N_j/N) x_j, \quad (2.16)$$

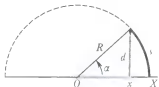


Fig. 4. Mean value depends on the variable over which averaging is performed

where $N = \sum_j N_j$, N_j being the number of identical terms in the sum (2.15), having the same value x_j . Since $(N_j/N) = \mathcal{P}_j$ is the probability that X assumes the value x_j , formula (2.16) for the mean value can be written in the following form:

$$\langle x \rangle = \sum_j \mathcal{P}_j x_j. \quad (2.17)$$

This formula defines the **expectation of a random quantity in terms of probability**.

MEAN VALUE OF A CONTINUOUS VARIABLE. This quantity is calculated with the help of a formula similar to (2.15). Let $\varphi(t)$ be a function of t . Then its mean value in the interval between t_0 and t_1 is given by the formula

$$\langle \varphi \rangle_t = \frac{1}{t_1 - t_0} \int_{t_0}^{t_1} \varphi(t) dt,$$

where the subscript t on the angle brackets indicating averaging shows the quantity over which the averaging is carried out. If it is required to show the interval (t_0, t_1) over which the averaging is performed, this can also be done on the left-hand side of the angle brackets. However, the variable over which the averaging is performed in most cases is known, and there is no need to indicate it by the appropriate subscripts. Figure 3 gives the geometrical interpretation of the mean value $\langle \varphi \rangle_t$.

It should be noted that the **mean value depends on the variable over which the averaging is carried out**. For example, when a material point moves along a semicircle, its mean distance from the diameter will be different (Fig. 4) if averaging is performed along the semicircle, from the value obtained by the averaging along the projection of this point on the diameter of the circle:

$$\langle d \rangle_s = \frac{1}{\pi R} \int_0^{\pi R} R \sin\left(\frac{s}{R}\right) ds = \frac{2R}{\pi},$$

$$\langle d \rangle_x = \frac{1}{2R} \int_{-R}^R \sqrt{R^2 - x^2} dx = \frac{\pi R}{4}.$$

Expression (2.17) can be generalized for a continuously varying random quantity as follows:

$$\langle x \rangle = \int_{-\infty}^{\infty} x f(x) dx, \quad (2.18)$$

where $f(x)$ is the probability density of the distribution of the variable x .

VARIANCE. The "spread" of a quantity about its mean is characterized by its variance which is defined as the mean square deviation of the quantity under consideration from its mean and is given by the formula

$$\begin{aligned} \sigma^2 &= \langle (x - \langle x \rangle)^2 \rangle = \langle [x^2 - 2x\langle x \rangle + (\langle x \rangle)^2] \rangle \\ &= \langle x^2 \rangle - (\langle x \rangle)^2. \end{aligned} \quad (2.19a)$$

The square root of the variance is called the **standard deviation** or the **root-mean-square deviation**.

Taking (2.17) and (2.18) into account, we can elaborate formula (2.19a) as follows:

(a) for a discrete random quantity

$$\sigma^2 = \sum_j (x_j - \langle x \rangle)^2 \mathcal{P}_j; \quad (2.19b)$$

(b) for a continuous random quantity

$$\sigma^2 = \int_{-\infty}^{\infty} (x - \langle x \rangle)^2 f(x) dx. \quad (2.19c)$$

PROBABILITY DISTRIBUTION FUNCTION. The probability that a random variable x assumes values smaller than a given number x_0 , i.e. $x < x_0$, is given by

$$\mathcal{P}(x < x_0) = F(x_0) = \sum_{x_j < x_0} \mathcal{P}_j. \quad (2.20)$$

The function $F(x_0)$ defined by this formula is called the **probability distribution function**.

For a continuous variable, the probability distribution function is represented, in accordance with (2.20), through the probability density $f(x)$ as follows:

$$F(x_0) = \int_{-\infty}^{x_0} f(x) dx. \quad (2.21)$$

It follows from this formula that

$$f(x) = dF(x)/dx. \quad (2.22)$$

With the help of this formula, we can rewrite the expressions containing $f(x) dx$ by considering that $dF(x) = f(x) dx$. For example, formula (2.18) can be rewritten as follows:

$$\langle x \rangle = \int_{-\infty}^{\infty} x dF(x). \quad (2.23)$$

Taking into account (2.20) and (2.21), we can express the probability of a random variable x assuming a value from the interval $x_1 < x < x_2$ in the following form:

$$\mathcal{P}(x_1 < x < x_2) = \int_{x_1}^{x_2} f(x) dx = \int_{x_1}^{x_2} dF(x) = F(x_2) - F(x_1). \quad (2.24)$$

Example 2.1. An urn contains $n = 30$ white and $m = 10$ black identical balls. The balls are mixed thoroughly. Find the probabilities $\mathcal{P}(b)$ and $\mathcal{P}(w)$ of drawing a white and a black ball in one trial. Verify the normalization condition. Find the probability of successively drawing two black balls, two white balls, a white ball and a black ball, and a black ball and a white ball respectively, if, after the first trial, the ball is (a) returned and (b) not returned to the urn.

Since there are no circumstances favouring the extraction of any specific ball (black or white), the probability of extracting a ball in a trial is the same and is equal to $1/(n + m)$. Consequently, according to the probability summation rule, the probability of extracting any black ball in a trial is equal to

$$\mathcal{P}(b) = \underbrace{1/(n + m) + 1/(n + m) + \dots + 1/(n + m)}_{n \text{ times}} = n/(n + m) = 0.75. \quad (2.25a)$$

Similarly, the probability of extracting a white ball is

$$\mathcal{P}(w) = m/(n + m) = 0.25. \quad (2.25b)$$

Since these two events form a complete set of all possible outcomes of a trial, they must satisfy the probability normalization condition. The verification of this condition will simultaneously serve as the verification of the correctness of the above calculations:

$$\mathcal{P}(b) + \mathcal{P}(w) = n/(n+m) + m/(n+m) = 1. \quad (2.25c)$$

If two balls are extracted successively, there will be four possible outcomes: white and white (ww), black and black (bb), white and black (wb), and black and white (bw). Since these four outcomes form a complete set of possible outcomes, their probabilities must satisfy the normalization condition:

$$\mathcal{P}(ww) + \mathcal{P}(bb) + \mathcal{P}(wb) + \mathcal{P}(bw) = 1. \quad (2.26)$$

If after the first trial the extracted ball is returned to the urn, the probability of extracting a ball of a certain colour in the second trial will be the same as for the first trial. Hence,

$$\left. \begin{aligned} \mathcal{P}_1(w) &= \mathcal{P}_2(w) = n/(n+m) = 0.75, \\ \mathcal{P}_1(b) &= \mathcal{P}_2(b) = m/(n+m) = 0.25. \end{aligned} \right\} \quad (2.27)$$

The probability of the outcome of the second trial does not depend on the result of the first trial, i.e. the events of the first and the second trials are independent. Hence, for the probability of the outcome of two successive trials, we obtain, in accordance with the probability multiplication rule,

$$\mathcal{P}(ww) = \mathcal{P}_1(w) \mathcal{P}_2(w) = [n/(n+m)]^2 = 0.5625;$$

$$\mathcal{P}(bb) = \mathcal{P}_1(b) \mathcal{P}_2(b) = [m/(n+m)]^2 = 0.0625;$$

$$\mathcal{P}(wb) = \mathcal{P}_1(w) \mathcal{P}_2(b) = [n/(n+m)] [m/(n+m)] = 0.1875;$$

$$\mathcal{P}(bw) = \mathcal{P}_1(b) \mathcal{P}_2(w) = [m/(n+m)] [n/(n+m)] = 0.1875.$$

The normalization condition has the form

$$\left(\frac{n}{n+m}\right)^2 + \left(\frac{m}{n+m}\right)^2 + \frac{nm}{(n+m)^2} + \frac{mn}{(n+m)^2} = 1.$$

If after the first trial the extracted ball is not returned to the urn, the result of the second trial will depend on the result of the first trial, i.e. in the second trial we are dealing with conditional probability. As in the previous case, the probabilities of extracting a white or a black ball in the first

?

1. Give the definition of probability.
2. What property of an aggregate of events makes the probability normalization possible?
3. What is the significance of the quantity distinguishing the probability summation formula for the general case from the corresponding formula for mutually exclusive events?
4. Does the mean value depend on the variable over which the averaging is performed? Give examples supporting the answer.
5. What is a standard deviation and what does it characterize?

trial are given by formulas (2.25a) and (2.25b). The conditions are altered for the second trial. If a white ball was extracted in the first trial, the probability of extracting a white ball in the second trial will be

$$\mathcal{P}_2(w/w) = (n-1)/(n+m-1) = 0.744, \quad (2.28)$$

since for the second trial the urn will contain only $n+m-1$ balls of which $n-1$ are white. Similarly, the conditional probabilities of other outcomes of the second trial will be given by the formulas

$$\mathcal{P}_2(b/b) = (m-1)/(n+m-1) = 0.310;$$

$$\mathcal{P}_2(w/b) = n/(n+m-1) = 0.769;$$

$$\mathcal{P}_2(b/w) = m/(n+m-1) = 0.256.$$

The conditional probabilities do not satisfy the normalization condition in the second trial, since the corresponding events are not mutually exclusive. For example, a white ball may be drawn after a black ball, or after a white ball, and so on.

The probability of successively extracting two white balls is given, in accordance with (2.11), by

$$\begin{aligned} \mathcal{P}(ww) &= \mathcal{P}_1(w) \mathcal{P}_2(w/w) = \frac{n}{n+m} \frac{n-1}{n+m-1} \\ &= 0.75 \cdot 0.744 = 0.558. \end{aligned}$$

Similarly,

$$\begin{aligned} \mathcal{P}(bb) &= \mathcal{P}_1(b) \mathcal{P}_2(b/b) \\ &= [m/(n+m)] [(m-1)/(n+m-1)] = 0.25 \cdot 0.310 \\ &= 0.0775; \end{aligned}$$

$$\begin{aligned} \mathcal{P}(wb) &= \mathcal{P}_1(w) \mathcal{P}_2(b/w) = [n/(n+m)] [m/(n+m-1)] \\ &= 0.75 \cdot 0.256 = 0.192; \end{aligned}$$

$$\begin{aligned} \mathcal{P}(bw) &= \mathcal{P}_1(b) \mathcal{P}_2(w/b) = [m/(n+m)] [n/(n+m-1)] \\ &= 0.25 \cdot 0.769 = 0.192. \end{aligned}$$

The events of two trials constitute a complete system of mutually exclusive events and must satisfy the normalization condition. Let us verify this:

$$\begin{aligned} &\frac{n(n-1)}{(n+m)(n+m-1)} + \frac{m(m-1)}{(n+m)(n+m-1)} \\ &+ \frac{nm}{(n+m)(n+m-1)} + \frac{mn}{(n+m)(n+m-1)} = 1. \end{aligned}$$

At the same time, we have verified that all possible outcomes of two trials have been taken into account during calculations. The fact that the sum of the probabilities of individual trials is equal to unity, i.e.

$$0.558 + 0.0775 + 0.192 + 0.192 = 1.0195 \approx 1,$$

may serve as a verification of the correctness of the results of numerical calculations. The above result confirms, to within the accuracy of calculations, the correctness of the numerical values for the probabilities of the individual outcomes of trials.

Since the number of white balls in the urn is nearly thrice the number of black balls, the probability of events in which at least one of the extracted ball is white is considerably higher than the probability of the event when a white ball is not extracted, i.e. when two black balls are extracted. In nearly 60% of cases, two white balls will be extracted, while a black and a white ball will be extracted in about 40% of the cases. In less than 10% of cases can two black balls be extracted.

Example 2.2. Many years of meteorological observations at a certain place showed that 20% of the days in November are cloudless, while it rains on 20% of the cloudy days. Find the percentage of rainy days in November and the probability of forecasting rain on a certain day.

The probability $\mathcal{P}(s)$ of a sunny (cloudless) day is equal to 0.2. Consequently, the probability of a cloudy day in $\mathcal{P}(c) = 1 - \mathcal{P}(s) = 0.8$. It can rain only on a cloudy day, hence the probability of a rainy day, according to the formulation of this problem, is conditional. The probability that a day is rainy provided that it is cloudy is $\mathcal{P}(r/c) = 0.2$. The probability of rain on a sunny day is $\mathcal{P}(r/s) = 0$. Hence, the probability of a rainy day is obtained from the probability multiplication rule:

$$\mathcal{P}(cr) = \mathcal{P}(c)\mathcal{P}(r/c) = 0.8 \cdot 0.2 = 0.16,$$

i.e. 16% of the days in November are rainy days at this place.



We cannot observe the microscopic state of a many-particle system for the same reasons which make a dynamic description of their motion impossible. The more so, because we are not in a position to observe the variation of the microscopic states. How can we prove that such systems exist and vary? We can observe and measure various parameters characterizing the state of individual particles as well as their interaction with the system as a whole. This leads to the conclusion about the existence of the microscopic state of a system of particles and about the variation of such states.

Sec. 3. MACROSCOPIC AND MICROSCOPIC STATES OF A SYSTEM

The definitions of the macroscopic and microscopic states of a system are formulated and the relation between them is analysed. The concept of a statistical ensemble is introduced, and the microcanonical ensemble is described.

DEFINITION OF A SYSTEM. A system is a finite region in space containing the physical objects of investigation. The boundary of a system may be real (for example, the walls of a vessel) or imaginary (drawn mentally in the space). It may be fixed or movable. A boundary may be penetrable or impenetrable for a substance, and it may or may not be able to transport energy. In the former case, it is classified according to the forms of energy which can be transported across it.

A system is characterized not only by the properties of its boundary, but also by the physical or chemical properties of the substance in the space occupied by it. As and when required, we shall classify systems according to these criteria. The first system which we shall consider here is an ideal gas. By an ideal gas we mean an aggregate of point particles having a finite mass, colliding with one another according to the laws of perfectly elastic collisions between balls. There are no other means of interaction between particles, i.e. there are no forces of interaction between particles at a finite distance.

THE MACROSCOPIC STATE. Suppose that an ideal gas is confined within a volume V . We assume that the collisions of the particles with the vessel walls are perfectly elastic, and that the mass of the vessel is very large, so that the impact of particles against its walls do not change its state of motion. Thus, the gas contained in a volume V does not exchange energy with the material bodies outside the volume V or, in other words, it is isolated. Under these conditions, the gas in a vessel is isolated from all external influences and all variations in it are due to internal reasons.

After a sufficiently large time interval, during which the system is left entirely to itself, the gas attains a steady state and no further variations in it will occur with time. In this statement the meaning of "a sufficiently large time interval" or "the gas attains a steady state" is not clear. An exact quantitative interpretation of these expressions and other related concepts can be given only at a later stage when the behaviour of the gas has been studied. For the present, it is sufficient to confine ourselves to the intuitive concept that irrespective of the initial pressure and temperature distribution in a gas, they stabilize after a certain interval over the entire volume and will then remain constant in time, i.e. the gas attains a steady state.



If a system is not isolated, it can be in a steady state which is not an equilibrium state.

A microcanonical ensemble is an aggregate of identical isolated systems having the same energy.

"A sufficiently large time interval" is an interval during which an equalization of temperatures and pressures over the entire volume takes place. It can be estimated from an investigation of transport phenomena. Here, we shall just remark that the equalization of pressure is determined by the velocity of sound v_s . If L is the linear dimension of the vessel, the equalization time for pressures is equal to L/v_s in order of magnitude. Since $v_s = 330$ m/s under normal atmospheric conditions, this time for $L \approx 1$ m is approximately equal to 3×10^{-3} s. Judging by our macroscopic perception of time, it can be considered to be quite small. However, if we proceed from the microscopic properties of molecular motion, this time is quite long. For example, a given molecule undergoes about 10^9 collisions per second with other molecules under normal conditions. Hence, "from the point of view of this molecule", the interval of 3×10^{-3} s is quite large, since the molecule undergoes over a million collisions with other molecules during this period. The state of a gas, characterized by its pressure, temperature, and volume, is called the macroscopic state.

THE EQUILIBRIUM STATE. The macroscopic steady state of a gas isolated in volume V from the external medium is called the equilibrium state. In this case, its macroscopic characteristics, viz., its pressure, temperature, and volume, retain their constant values in time, the pressure and temperature being the same in all parts of the volume. By "parts of volume" we mean sufficiently large parts containing a very large number of particles.

The constraint regarding the isolation of the system is important in the definition of equilibrium state. If the system is not isolated, it can have a steady state which is not an equilibrium state. If, for example, different parts of the walls of a vessel containing a gas are maintained at different constant temperatures with the help of external heat sources, a steady state will be established in the gas, i.e. the state of the gas will not change with time. This state, however, will not be the equilibrium state. In this case, the pressure in all parts of the volume will be the same, although the temperature will be different in different parts.

THE MICROSCOPIC STATE. The most complete information about a gas can be obtained by ascertaining the positions and velocities of all its particles (see Sec. 1). Let us label the particles of a gas by the indices $i = 1, 2, \dots, n$. This means that the volume under consideration contains n particles in all. This is a very large number. If the volume $V = 1$ cm³, $n = 2.7 \times 10^{19}$ particles under normal atmospheric conditions. The state of a gas, characterized by

?

1. Estimate the order of the interval of time for equalization of pressure in a gas.
2. Which quantities characterize the macroscopic and microscopic states of a gas?
3. What is the general nature of relations between macroscopic and microscopic states?

the positions and velocities of all its particles, is called the microscopic state.

Consequently, the microscopic state of a gas is characterized by $6n$ numbers, viz. $3n$ coordinates (x_{i1}, y_{i1}, z_{i1}) of all the particles and $3n$ components $(v_{xi1}, v_{yi1}, v_{zi1})$ of their velocities. These numbers should be treated as random quantities (see Sec. 1).

The macroscopic state is characterized by three quantities, viz., pressure, temperature, and volume. In the steady state, these quantities are constant. However, the particles in a gas are in motion even in the steady state and hence its microscopic states keep changing continuously. Thus, an enormously large number of microscopic states correspond to each macroscopic state. In other words, a given macroscopic state is realized through an enormously large number of microscopic states.

The statistical physics aims at establishing a relation between the microscopic and macroscopic states of systems.

THE STATISTICAL ENSEMBLE OF SYSTEMS. The method of system ensembles (see Sec. 2) is convenient for analyzing the questions of statistical physics. Let us consider an extremely large number N of vessels which are exactly identical and have a volume V each. Each of the vessels contains an identical number n of identical particles. A vessel containing such particles is called a statistical system, while the aggregate of identical statistical systems is called a statistical ensemble.

We are not interested in how the particles move or what points of the corresponding vessels are occupied by these particles at a certain initial moment of time. Our aim is to study the microscopic and macroscopic states of the individual systems of the ensemble after a sufficiently large interval of time, the term "sufficiently large interval of time" being understood in the sense described above.

It is clear from the above description that the same macroscopic state is realized in a large number of systems of an ensemble, which are in different microscopic states.

THE MICROCANONICAL ENSEMBLE. A microcanonical ensemble consists of identical isolated systems having the same energy. Besides microcanonical ensembles, statistical physics also considers canonical ensembles (see Sec. 7) as well as other ensembles. The method of ensembles was introduced into statistical physics in 1902 by the American physicist Gibbs (1839–1903).

Sec. 4. THE EQUAL PROBABILITY POSTULATE AND THE ERGODIC HYPOTHESIS

The arguments in favour of equiprobability postulate are analysed. The physical content of the ergodic hypothesis is considered, and the relationship between the equiprobability postulate and the ergodic hypothesis are revealed.

DISTINCTION BETWEEN MICROSCOPIC STATES. It has just been mentioned that even when a system remains in the same macroscopic state, its microscopic states keep changing incessantly. Since the microscopic states of a system are characterized by continuously varying values of coordinates and velocities of particles, one can naturally ask: what amount of variation of these quantities is sufficient to consider that the microscopic state has changed? What is the meaning of the expression "a system is in the given state" if this statement refers just to a moment of time which itself has no duration but simply separates the past from the future? Naturally, such a representation is equivalent to the investigation of a system which is beyond time and is not compatible with our physical concepts about the development of a process in space and time. It can be easily seen that these questions are equivalent to those posed by the Greek philosopher Zeno concerning stoicism. The paradoxes, or aporias, of Zeno formed the subject of numerous discussions and reflections by most of the leading intellectuals for over two thousand years. Their significance became clear only after the appearance of the mathematical set theory and quantum mechanics. The difficulties in distinguishing between microscopic states can be satisfactorily overcome only by using the quantum-mechanical concepts. Here, we shall describe a somewhat artificial (and not quite satisfactory) method which was used in classical statistical physics.

The justification for using such an approach is that it led to some important results even within the framework of the classical statistical physics. Later, these results were confirmed more than satisfactorily with the help of quantum statistics.

It is well known that atoms and molecules have certain dimensions. Their diameter d is of the order of 10^{-10} m, and so each atom or molecule occupies a volume $d^3 \approx 10^{-30}$ m³. The expression "occupies a volume" means that if a certain particle is present in this volume, no other particle can be present in this volume. Hence, a particle is considered to have changed its position if it goes over from the volume occupied by it to another volume which it is capable of occupying. Under such a representation, the entire volume V occupied by a gas can be assumed to be divided into cells, each having a volume d^3 , which can be occupied by individual particles. The motion of particles involves an abrupt transition from one cell to another. The duration of

stay of a particle in each cell is of the order of d/v , v being the velocity of the particle.

It is now possible to distinguish between microscopic states on the basis of the positions of particles. Depending on the positions of particles in space, a microscopic state is characterized by a certain distribution of all the particles over cells into which the volume under consideration is divided. The change in the microscopic state of a system should be seen as a transition of particles from one cell to another. In order to use such a concept, it is not necessary to assume that the particles of a gas really have geometrical dimensions of the order d . As before, we can assume that the particles of an ideal gas have zero dimensions, but that their laws of motion are such that only one particle can exist in a cell at one time. It is this concept that we shall be using in this book while considering questions concerning an ideal gas.

According to the above considerations, there are $N = 1/d^3 \simeq 10^{30}$ cells in 1 m^3 . On the other hand, the number of particles in this volume under normal conditions is $n = 2.7 \times 10^{25}$. This means that under normal conditions, there is one particle for every $N/n \simeq 4 \times 10^4$ cells. Consequently, most of the cells are empty and only a few of them are occupied by particles. If the cells are arranged in the form of cubes, one particle will occupy a cube consisting of 40000 cells. More than 30 cells are situated along each side of such a cube. Consequently, the mean distance between occupied cells is more than 30 times the linear dimensions of a cell.

Let us now find a method of distinguishing between the microscopic states on the basis of velocities. This problem is reduced to finding a change in velocity for which the state of motion of a particle can be considered to have changed. In other words, we must construct "velocity cells" for velocities in the same way as it was done for coordinates. This problem could not be solved by the classical theory, and had to await the advent of quantum mechanics. Classical mechanics had to remain content by assuming that such a subdivision of states according to velocities (or momenta) is possible and that it is possible, in principle, to count the number of states, although it was unable to indicate how this can be actually done. Such a description was found to be satisfactory in most cases, since "the number of microscopic states according to momentum" was either eliminated in the final results, or the numerical counting could be replaced by integration over continuous variables by passing to the limit.

It was first shown by quantum mechanics that a particle cannot occupy a certain volume in space and a certain "volume" in velocities. Its spatial and velocity properties are

interrelated and cannot be isolated from each other. Moreover, the motion of a particle is defined not by its velocity $\mathbf{v}$, but rather by its momentum $\mathbf{p}$. The volume of cells which can be occupied by one particle is determined not in the space of coordinates or space of momenta, but in the space of coordinates and momenta, which is called the phase space. The volume of a cell occupied by a particle in this space is equal to

$$(\Delta x \Delta y \Delta z)_0 (\Delta p_x \Delta p_y \Delta p_z)_0 = (2\pi\hbar)^3, \quad (4.1)$$

where $\hbar = 1.05 \times 10^{-34} \text{ J} \cdot \text{s}$ is the Planck constant. It should be noted that in optics and spectroscopy, the Planck constant $h = 2\pi\hbar$ is frequently used instead of $\hbar$. This is so because it is a more convenient form when we are dealing with the frequency $\nu = \omega/(2\pi)$ instead of the circular frequency, since $\hbar\omega = h\nu$.

The quantum-mechanical approach described by (4.1) for considering microscopic states will be used somewhat later in this book. First let us confine ourselves to the analysis of different microscopic states in ordinary space, avoiding an explicit analysis of states in the momentum space and remaining content with the knowledge that this can be done if required. The methods and concepts used in this case are quite simple and clear on the one hand, and on the other hand, can be easily extended to the phase space.

THE EQUIPROBABILITY POSTULATE. The particles in each system of a microcanonical ensemble are assumed to be numbered, just as the cells in which particles can be located. At a certain moment of time, a certain particle may be found in different cells in different systems of an ensemble. If a sufficient amount of time has elapsed from the initial moment, and if all the systems of the ensemble have "forgotten" their initial state, the cell in which a specific particle may find itself at a particular moment is a random one. There are no motives for the particle under consideration to be present in a certain cell in preference to another. All the cells are equivalent and all the positions of the particle are equally probable. If an ensemble contains a very large number N_s of systems, the number of systems in which the particle under consideration will appear in cell 1 will be equal to the number of systems in which it will appear in cell 2, and so on. In other words, all possible positions for the particle are equally probable. A microscopic state is characterized by the position of all N particles comprising the system, i.e. by the specific distribution of these particles over cells into which the volume is divided.

!

Although all particles are identical in terms of their internal characteristics, a certain "hierarchy" exists among the particles at all instants of time. For example, some particles have a higher kinetic energy than the others, some particles are closer to the centre of the vessel in which they are contained while others are closer to the walls, and so on. However, the "hierarchy" positions of the particle rapidly vary, and there are no hereditary kings or perpetual beggars. Over a sufficiently large interval of time, each particle appears at all the steps of the "hierarchy" ladder. Moreover, all particles spend, on the average, the same amount of time at each step of the ladder.

Since all the cells are equally probable for all the particles, it is logical to assume that all distributions of particles over the cells are also equivalent. This means that all the microscopic states are equally probable. Hence, for example, a system in which all the particles are gathered in one corner of the volume under consideration and occupy all n cells in this corner in a certain way will be encountered in the ensemble the same number of times as a system in which particles are found in all corners of the volume and correspondingly occupy n cells, again in a certain way.

The statement about equally probable microscopic states is called the **equiprobability postulate**.

The above discussion, however, does not constitute a proof of this statement.

At present, such a general proof does not exist, and that is why this statement is called a postulate. It is of extreme importance in statistical physics.

CALCULATION OF MEAN VALUES OVER AN ENSEMBLE. Let us consider some quantity associated with a certain particle, for example, the square of its coordinate. The arrangement of the coordinate system is arbitrary, and the only important point is that the coordinates should be identical for all systems of the ensemble (Fig. 5). We shall denote the coordinate of a particle in the i -th system of a statistical ensemble by the subscript i . Then, by definition of the mean, we get

$$\langle x^2 \rangle_a = \frac{1}{N_a} \sum_{i=1}^{N_a} x_i^2. \quad (4.2)$$

The index a in this equality means that the mean of the quantity under consideration is taken over the entire ensemble, N_a is the number of systems in the ensemble, and x_i is the coordinate of a particle in the i -th system of the ensemble. The number of cells in each system of the ensemble is equal to $N \simeq 10^{30}$, while the number N_a of systems in the ensemble is assumed to be much larger ($N_a \gg N$). Hence, it can be assumed that the number of systems of the ensemble, in which a particle is present in the j -th cell, is large. Suppose that this number is equal to N_{aj} . From the definition (2.1) of the probability in terms of frequency, we obtain the probability of finding a particle in the j -th cell:

$$\mathcal{P}_j = N_{aj} / N_a. \quad (4.3)$$

We transform the sum in (4.2) in such a way that the terms corresponding to the same cell in different systems of the

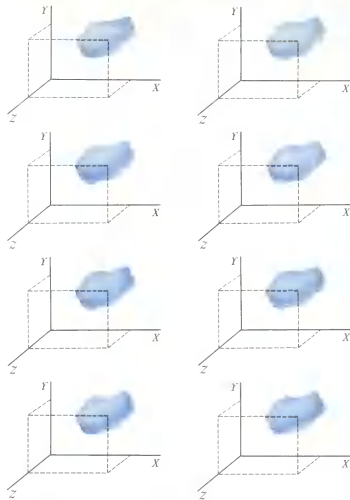


Fig. 5. Statistical ensemble

ensemble are grouped together. Since, as mentioned earlier, a particle appears in the j -th cell in N_{aj} systems of the ensemble, we obtain

$$\sum_{i=1}^{N_s} x_i^2 = \sum_{j=1}^N N_{aj} x_j^2, \quad (4.4)$$

where x_j is the x -coordinate of the j -th cell, N_{aj} is the number of systems in the ensemble containing a particle in the j -th cells, and N is the number of cells in each system of the statistical ensemble.

With the help of (4.4) and (4.3), we can express (4.2) in the

following form:

$$\langle x^2 \rangle_a = \frac{1}{N_a} \sum_{j=1}^N N_{aj} x_j^2 = \sum_{j=1}^N \mathcal{P}_j x_j^2, \quad (4.5)$$

where x_j is the x coordinate of the j -th cell, and $\mathcal{P}_j$ is the probability of a particle being present in this cell. This expression corresponds to formula (2.17) for the mathematical expectation of a random quantity. The ensemble of systems is not mentioned in explicit terms of the right-hand side of this expression. The concept of the ensemble is contained in this formula in an implicit form through the probability $\mathcal{P}_j$ of finding a particle in the j -th cell. Although formulas (4.2) and (4.5) are equivalent, it is sometimes easier to compute the mean over an ensemble by using formula (4.5).

CALCULATION OF MEAN VALUES OVER TIME. Let us track the position of the particle under consideration in one of the systems of the ensemble over a very large interval of time ($T \rightarrow \infty$) and find the mean value of the square of the x coordinate of this particle. In our model, the coordinate $x(t)$ of this particle changes abruptly as the particle goes over from one cell to another. Then as per definition of the mean over time, we can write

$$\langle x^2 \rangle_t = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T x^2(t) dt. \quad (4.6)$$

We denote the successive jumps of the particle through the index i ; x_i is the coordinate of the cell into which the particle arrives during its motion as a result of the i -th jump; and Δt_i is the duration of the stay of the particle in this cell after its arrival there as a result of the i -th jump. On the basis of this, the integral in formula (4.6) can be transformed as follows:

$$\int_0^T x^2(t) dt = \sum_{i=1}^m x_i^2 \Delta t_i, \quad (4.7a)$$

where m is the number of jumps in an interval of time T :

$$\sum_{i=1}^m \Delta t_i = T. \quad (4.7b)$$

For a very large value of time T ($T \rightarrow \infty$), a particle arrives at each cell several times. Thus, the time spent by it in the

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Suppose that we are watching a film showing a fisherman catch a fish on his fishing-rod. At certain intervals of time, the fisherman extracts the hook from the water, removes the fish, and throws it into a bucket containing water. After this, he puts the bait on the hook and throws it back into the water. We can measure the duration of these intervals with the help of a chronometer. Obviously, the total duration of these time intervals, divided by the duration of the entire film, is equal to the number of frames containing pictures from the moment of extraction of the hook from the water to the instant of its being thrown into the water, divided by the total number of frames in the film. This is the main part of the ergodic hypothesis, but not all of it. What else remains to be proved?

j -th cell over a period T is given by

$$T_j = \sum \Delta t_i, \quad (4.8)$$

where the sum is taken over all i 's corresponding to the j -th cell.

Formula (4.7b) can be transformed as follows with the help of (4.8):

$$T = \sum_{j=1}^N T_j. \quad (4.9)$$

Taking into account (4.7a), (4.7b), and (4.8), we can rewrite (4.6) in the following form:

$$\langle x^2 \rangle_t = \lim_{T \rightarrow \infty} \frac{1}{T} \sum_{j=1}^N T_j x_j^2 = \sum_j \tilde{\mathcal{P}}_j x_j^2, \quad (4.10)$$

where

$$\tilde{\mathcal{P}}_j = \lim_{T \rightarrow \infty} (T_j/T). \quad (4.11)$$

This is the duration of stay of the particle in the j -th cell relative to the entire period of time. In accordance with the definition (2.2c) of probability, $\tilde{\mathcal{P}}_j$ is the probability of the particle being present in the j -th cell.

THE ERGODIC HYPOTHESIS. It can be asked whether the probability (4.11) is equal to the probability (4.3).

The discussion carried out above cannot provide an answer to this question, although intuitively it seems obvious that it is true. The statement

$$\tilde{\mathcal{P}}_j = \mathcal{P}_j, \quad (4.12)$$

where $\mathcal{P}_j$ and $\tilde{\mathcal{P}}_j$ are defined by formulas (4.3) and (4.11), respectively, is called the **ergodic hypothesis**. It can be expressed in another form if we write, on the basis of (4.10), (4.5), and (4.12),

$$\langle x^2 \rangle_a = \langle x^2 \rangle_t, \quad (4.13)$$

which means that the mean over the ensemble is equal to the mean over time. So far, there is no proof of the validity of

this statement in the general case, and it is taken as one of the basic assumptions of statistical physics.

This hypothesis was first proposed by Boltzmann (1844–1906) in 1871. Later, Maxwell in 1879 analyzed the possibility of replacing the mean over time by the mean over the ensemble.

We have illustrated the idea of the ergodic hypothesis by an artificial example of “one-particle states” in order to reveal its essence in the most visual form. However, we actually deal with the state of a system consisting of an enormous number n of particles. In this case, the ensemble of systems which is investigated at a certain instant of time is an aggregate of microscopic states of the system. The ergodic hypothesis implies that this aggregate involves all the states of the system which are compatible with the possible motion of particles in space and with the law of conservation of energy (if we also consider the momentum distribution of particles). Any system from the ensemble will pass through all possible microscopic states during a sufficiently large interval of time, its relative stay in each of the microstates being equal to the relative number of systems in the ensemble, which are in a given state. These two assumptions lead to the conclusion that the mean over the ensemble is equal to the mean over time. This statement can serve as the formulation of the ergodic hypothesis.

In other words, the ergodic hypothesis can be expressed by the statement that **a system, which begins its motion from any state must attain a state infinitely close to some other state in accordance with the law of conservation of energy.**

The reservation that a system attains a state infinitely close to any possible state and not the state itself is quite significant. Let us consider, for example, an ideal gas for which the ergodic hypothesis is obviously satisfied, and yet we can indicate some states of this system which are never attained. Suppose that the gas is contained in a cubic vessel, all the particles moving parallel to one of the edges. Suppose further that the particles are distributed in space in such a way that they do not collide with each other, but just with two opposite faces of the cube. In this state the system may stay for an infinitely long time, and it is impossible for even a single particle to deviate from the direction parallel to the chosen edge of the cube. Since the equations of mechanics governing the motion of the particles are reversible in time, the system cannot come to this state from other states in which the particles have velocities noncollinear with the selected edge of the cube. But this means that for an ideal gas (which can be assumed to be an ergodic system) there are



Equiprobability postulate is the statement about equal probability of different microscopic states. However, the probabilities of different macroscopic states drastically differ from each other.

Ergodic hypothesis states that in equilibrium, the ensemble average quantity is equal to the time average quantity.

states that cannot be attained. However, the system will certainly come infinitely close to these unattainable states.

THE RELATION BETWEEN THE EQUIPROBABILITY POSTULATE AND THE ERGODIC HYPOTHESIS. If we assume that the ergodic hypothesis is true, we can prove the equiprobability postulate by using the Liouville theorem in the classical case and the principle of detailed balance in the quantum case. This proof, however, is beyond the scope of this book.

Sec. 5. THE PROBABILITY OF A MACROSCOPIC STATE

The concept of thermodynamic probability is defined, and the probability of a macroscopic state is calculated on the basis of the general relation between microscopic and macroscopic states.

The connection between the equilibrium state and the most probable macroscopic state is established, and the binomial and Poisson distributions are introduced.

?

1. Which model of position and motion of gas molecules must be accepted in order to ascribe a definite meaning to the concept of variation of microscopic states?
2. Explain the meaning of different formulations of the ergodic hypothesis.
3. Give an example of an unattainable problem for the ergodic hypothesis of the state, which nevertheless is compatible with the law of conservation of energy.
4. What is the source of difficulty in counting the number of microscopic states in prequantum physics?

THE PROBABILITY OF A MACROSCOPIC STATE. It is established from a large number of microscopic states. If the parameters characterizing a given macroscopic state are known, we can in principle enumerate all the microscopic states which are compatible with these criteria and thus find the number of such states. Let us denote the number of microscopic states by Γ_α , where α describes the microscopic state. Of course, we can also describe the parameter of the macroscopic state to which Γ belongs in the form of an argument of Γ , for example, $\Gamma(x)$, or in any other way that may turn out to be convenient under the conditions of a particular problem. We denote by Γ_0 the total number of states attainable for a system in accordance with the ergodic hypothesis.

On the basis of the equal probability postulate for microscopic states and the definition (2.1) of probability we obtain the following expression for the probability $\mathcal{P}_\alpha$ of the macroscopic state under consideration

$$\mathcal{P}_\alpha = \Gamma_\alpha / \Gamma_0. \quad (5.1)$$

The number Γ_α of a microscopic states is also called the thermodynamic probability of a macroscopic state. This number does not represent probability in the mathematical sense since the probability is always equal to or less than unity, while Γ_α is a very large number. Nevertheless, it was termed (thermodynamic) probability, since it can be used to find the corresponding probability of a macroscopic state in accordance with formula (5.1).

The theory aims at determining the number of states appearing in formula (5.1). Of course, a direct count of the number of states is possible only in rare cases. Hence, in

most cases, the problem is to find the number of states without counting them, or even to find the probability $\mathcal{P}_z$ directly without knowing the number of states. Various methods for achieving this will be discussed later. In the case of an ideal gas, it is comparatively easy to directly count the number of microscopic states with the help of the spatial variables. It should be noted that neglecting the states obtained from a distribution of particles according to momentum does not impose any restrictions on the validity of the analysis of the spatial distribution of particles. Obviously, the distribution of particles according to coordinates (spatial cells) and momenta (momentum cells) can be treated as independent. Hence the total number of microscopic states of a system is equal to the product of the number of spatial microstates and the number of momentum microstates.

In the probability calculations for a certain macroscopic spatial distribution, the number of momentum states is the same whether we calculate the number of microscopic states through which the given macroscopic state has been accomplished, or the total number of microscopic states in the system. Hence, the number of momentum states appears as a multiplier in the numerator and denominator of (5.1) and is cancelled out. Thus, while calculating the probability of a macroscopic state, the symbols Γ_z and Γ in the formula stand only for the number of spatial microscopic states.

FORMULAS OF THE BASIC COMBINATION THEORY. In order to directly count the number of microscopic states, we must know some formulas of the permutation theory.

Suppose that we have n places and n different objects. One can ask: "In how many ways can these n different objects be arranged among these n places?". To answer this question, let us consider any one of the n different objects. There are n ways of putting this object at one of the n available places. For each of these n positions, there are $n - 1$ places at which the second object can be placed, and hence there are $n(n - 1)$ different ways of putting two objects at n different places. There are $n - 2$ places available for the third object for each of the $n(n - 1)$ positions of the first two objects, and hence there are $n(n - 1)(n - 2)$ different ways of arranging three objects among n places, and so on. Thus, n different objects can be arranged at n different places in

$$n(n - 1)(n - 2) \dots 1 = n! \quad (5.2)$$

different ways. For example, suppose that we have n identical chairs in a row and n different people who can be seated on these chairs. The number $n!$ is the total number of different

photographs that can be obtained by seating these people in different ways on the chairs. For example, three persons (a man, a woman, and a child) can be seated on three chairs in $3! = 6$ different ways.



Next, suppose that we have m different objects. In how many different ways can these m objects be arranged among n places? For each arrangement of m objects, there will be $n - m$ free places. If these $n - m$ places were to be occupied by different objects, there would be $(n - m)!$ different ways of filling these places for each fixed arrangement of m objects. If we sort out all the possible arrangements of m objects at n places and carry out $(n - m)!$ arrangements of $n - m$ different objects at the remaining $n - m$ places in each case, we obtain the total number of arrangements of $m + (n - m) = n$ different objects at n different places, i.e. $n!$. Hence, the required number of ways in which m objects can be arranged at n different places is

$$\mathcal{P}(n, n - m) = n! / (n - m)! \quad (5.3)$$

!

A system "does not know" its most probable macroscopic states. It goes over from one microscopic state to another without any preference for any state. However, a vast majority of transitions occur towards the equilibrium state, and hence it can be concluded that the completely random transitions from one microscopic state to another give rise to an orderly motion of the system to the equilibrium state.

We must clarify the meaning of the expression "different ways of arrangement". Returning to the above examples of photographs, we must understand that m is the number of different people, while n is the number of chairs on which these people can be seated. Then, $\mathcal{P}(n, n - m)$ indicates the number of different photographs, where by different photographs we mean not only the photographs in which the seating order is different, but also such photographs in which the people are seated in the same order but on different chairs. Hence, the photograph in which these people are seated in a certain order from left to right on the first m chairs (the chairs are all in one row) is different from the photograph in which the same seating order is maintained,

but the people now occupy chairs numbered from 2 to $m + 1$. For example, the number of ways in which two persons (a man and a woman) can be seated on three chairs ($n = 3$) is $3!/[(3 - 2)!] = 6$.



Suppose that the m objects required to be arranged at n places are identical and indistinguishable from one another. In this case, two permutations differing only in that two objects interchange their positions are considered to be identical. Hence, for each permutation of m objects there are $m!$ permutations which can be treated as identical. Consequently, in accordance with (5.3), the required number of ways will be

$$C(n, m) = n!/[m!(n - m)!]. \quad (5.4)$$

In this case, the arrangements are different if different combinations of places are occupied, irrespective of the combination of m objects occupying these places. Hence, the photograph in which m persons occupy seats from 1 to m is different from the one in which they occupy seats from 2 to $m + 1$, but is identical to the photograph in which they occupy the same seats from 1 to m , but the order in which they are seated is altered in some way. For example, two identical persons can be seated on three chairs in $3!/2!(3 - 2)! = 3$ different ways.



Finally, let us consider one more question. Suppose that we have n different objects. In how many different ways can we choose a group of m objects so that each group is different from the other in its composition? The order in which these objects are arranged inside the group is not important.

This problem can be solved as follows. If the group consists of only one object, we can form n different groups out of n objects. Groups consisting of two objects are formed in the following way: each of the n different objects combines with the remaining $n - 1$ objects and hence the total number of combinations is $n(n - 1)$.

However, combinations differing only in the order of the objects are taken to be identical. The number of possible permutations for two objects is $2! = 2$, and hence the total number of groups of two objects that can be formed out of n objects will be equal to $n(n - 1)/2!$. Continuing the argument, we come to the conclusion that the number of ways in which m different objects can be chosen from n different objects is

$$C(n, m) = \frac{n(n-1)(n-2) \dots [n-(m-1)]}{m!} \quad (5.5)$$

$$= \frac{n!}{m!(n-m)!}.$$

This formula is similar to (5.4), but its meaning and the sense of the quantities appearing in it are quite different.

Suppose that we have a group of three persons ($n = 3$). The "objects" forming the group are a man, a woman, and a child, and it is required to choose the subgroups.



Clearly, this group of "objects" satisfies the conditions for the applicability of formula (5.5). It should be recalled once again that sequence of the "objects" or their mutual positions are not important in the complete group or in the subgroups formed out of them. From this group of three persons, we can form subgroups of two persons each ($m = 2$). The total

number of such groups is equal to $3!/2!(3-2)! = 3$.



CALCULATIONS OF THE PROBABILITY OF A MACROSCOPIC STATE. Let V be the volume occupied by an ideal gas and n be the number of particles in this volume. The number of cells which can contain the particles is $N = V/d^3$, where $d^3 \approx 10^{-30} \text{ m}^3$. This is a very large number and the condition $N \gg n$ is always satisfied. Let us find the probability $\mathcal{P}(V_1, m)$ of such a macroscopic state of the system in which m particles are present in a certain fixed volume V_1 which is a part of the total volume V (see Fig. 6). According to the conditions of the problem, $V_1 \leq V$ and $m \leq n$. Besides, the volume V_1 must not be too small and must contain at least m cells which could be occupied by the m particles. The number of cells in the volume V_1 is $N_1 = V_1/d^3$, hence $N_1 \gg m$.

The total number of microscopic states is obviously equal to the number of ways in which n particles can be distributed among N cells. The particles are assumed to be distinguishable (for example, they can be numbered). This means that two microscopic states in which the particles occupy the same cells will be different if, say, two particles have interchanged their positions in some cells. Here, it should be remembered that the particles under consideration have exactly identical properties. Consequently, the properties of two microscopic states in which the particles have interchanged their positions must be exactly identical, and yet we consider these microscopic states to be different. This has a definite physical meaning. For example, the system requires a certain amount of time to pass these seemingly identical microscopic states. Thus, for the total number of microscopic states of a system, we get in accordance with formula (5.3):

$$\Gamma_0 = N!/(N-n)! \quad (5.6)$$

Let us calculate the number of microscopic states through which the macroscopic state, in which the volume V_1 contains m particles, is realized. We denote this number by $\Gamma(V_1, m)$. If the volume V_1 contains any m particles, the total number of microscopic states for them will be

$$\gamma(V_1, m) = N_1!/(N_1-m)! \quad (5.7)$$

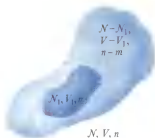


Fig. 6. To the calculation of the probability of a macroscopic state

The rest of the volume $V - V_1$ contains $n - m$ remaining particles. The number of microscopic states available for them is given by

$$\gamma(V - V_1, n - m) = (N - N_1)! / [N - N_1 - (n - m)]! \quad (5.8)$$

Thus, for m definite particles occupying the volume V_1 , the total number of microscopic states through which the macroscopic state is realized will be $\gamma(V_1, m) \gamma(V - V_1, n - m)$, since all the microscopic states are combined in the volume $V - V_1$ with each microscopic state in V_1 . However, the product $\gamma(V_1, m) \gamma(V - V_1, n - m)$ does not give all the microscopic states through which the macroscopic state is realized. This is only the number of microscopic states corresponding to a certain definite set of particles m in the volume V_1 . However, it can be seen from (5.4) that there are $n!/[m!(n - m)!]$ different ways in which m particles can be chosen from a total of n . Hence, the total number of microscopic states through which the macroscopic state is realized is

$$\Gamma(V_1, m) = \frac{n!}{m!(n - m)!} \gamma(V_1, m) \gamma(V - V_1, n - m). \quad (5.9)$$

Consequently, we obtain the following formula for the probability of a macroscopic state on the basis of (5.1):

$$\begin{aligned} \mathcal{P}(V_1, m) &= \frac{\Gamma(V_1, m)}{\Gamma_0} \\ &= \frac{n!}{m!(n - m)!} \frac{N_1!(N - N_1)!(N - n)!}{(N_1 - n)! [N - N_1 - (n - m)]! N!}. \end{aligned} \quad (5.10)$$

This also solves the problem of finding the probability of a macroscopic state, since all the quantities on the right-hand side of this formula are known. However, in order to make this formula easier to analyze, we must reduce it to a simpler form. This can be done by considering that the numbers appearing in this formula are quite large. Indeed, if a gas is under normal atmospheric conditions, $n \approx 10^{19}$, $N \approx 10^{24}$, and $N_1 = 10^{24}(V_1/V)$ for $V_1 = 1 \text{ cm}^3$. Hence, the number of cells in V_1 will also be extremely large, even if V_1 is only a small part of the volume V . For the conditions in which we are interested, we can put $N_1 \gg m$. This considerably simplifies formula (5.10).

STIRLING'S FORMULA. The following equality is satisfied for large n :

$$n! \approx (n/e)^n. \quad (5.11)$$

This relation, called Stirling's formula, is proved by proceeding from the equation

$$\ln n! = \ln 1 + \ln 2 + \dots + \ln n = \sum_{n=1}^n \ln n \Delta n, \quad \Delta n = 1. \quad (5.12)$$

Since Δn is assumed to be small for large values of n , we can replace the summation in (5.12) by integration:

$$\ln n! \simeq \int_1^n \ln n \, dn = n \ln n - n, \quad (5.13)$$

where we have neglected unity on the right-hand side, since it is small in comparison with n . Taking antilogarithms, we arrive at Eq. (5.11).

FORMULA FOR THE PROBABILITY OF A MACROSCOPIC STATE. All factorials in (5.10) must be expressed in terms of powers in accordance with (5.11). When using Stirling's formula, we must remember that $N_1 \gg m$, $N - N_1 \gg n - m$, and $N \gg n$. For example,

$$\begin{aligned} (N_1 - m)! &= \left(\frac{N - m}{e} \right)^{N_1 - m} \\ &= \left(\frac{N_1}{e} \right)^{N_1 - m} \left(1 - \frac{m}{N_1} \right)^{N_1 - m} = \left(\frac{N_1}{e} \right)^{N_1 - m} e^{-m}, \end{aligned}$$

where $\lim_{n \rightarrow \infty} (1 + x/n)^n = e^x$.

Other factorials are calculated in the same way. Consequently, formula (5.10) assumes the form

$$\begin{aligned} \mathcal{P}(V_1, m) &= \frac{n!}{m!(n-m)!} \frac{N_1^m (N - N_1)^{n-m}}{N^n} \\ &= \frac{n!}{m!(n-m)!} \left(\frac{N_1}{N} \right)^m \left(1 - \frac{N_1}{N} \right)^{n-m}. \end{aligned} \quad (5.14)$$

The meaning of this formula is quite simple: $p = (N_1/N) = (V_1/V)$ is the probability of finding a particle in the volume V_1 , while $q = 1 - N_1/N = 1 - p$ is the probability of finding the particle in the remaining volume $V - V_1$. Naturally, $p + q = 1$, since the particle must be either in the volume V_1 or in the volume $V - V_1$.

Using the probabilities p and q of finding a particle in volumes V_1 and $V - V_1$, we can write formula (5.14) in a more

convenient form:

$$\mathcal{P}(V_1, m) = \frac{n!}{m!(n-m)!} p^m q^{n-m}. \quad (5.15a)$$

This distribution is called binomial. In this definition of the binomial distribution the volume V_1 is immaterial, since it was chosen only in order to graphically illustrate the probability p for an individual particle to be found in this volume. The meaning of this definition is independent of the choice of volume V_1 , which is reflected by the absence of V_1 in the explicit form on the right-hand side of formula (5.15a).

Let us give a more general definition for the binomial distribution. Suppose that we make a certain experiment concerning the occurrence of a certain event. It is assumed that in each trial, an event either occurs or does not occur, and that there is no third choice. By way of an example, let us consider the drawing of balls from an urn. The urn contains a certain number of balls of different colours. The experiment consists in drawing a ball out of the urn at random. After the colour of the drawn ball is known, the ball is returned to the urn, and all the balls are then thoroughly mixed so that the next event occurs in the same conditions as the previous event. In other words, the outcome of an event must not depend on the outcome of the previous event, and the probability of the outcome of an individual trial must be constant. Suppose that the event under consideration is the drawing of a black ball out of the urn. We denote by p the probability of occurrence of this event as a result of an individual trial. Then $q = 1 - p$ will be the probability that such a ball will not be drawn as a result of this trial.

Let us determine the probability that a certain event occurs m times as a result of n trials. To begin with, let us find the probability that the event will occur m times in a certain order, for example,

$$\underbrace{(+)(+)(-)(+)(-)(-)(-)(+)...}_{m \text{ events, } n \text{ trials}}, \quad (*)$$

where $(+)$ means that the event has occurred, and $(-)$ means that the event has not occurred in a certain trial. The probability of realizing the sequence of events $(*)$ is obtained from the general probability multiplication rule:

$$pp(1-p)p(1-p)(1-p)p \dots = p^m (1-p)^{n-m},$$

since the event under consideration occurs m times as a result of n trials. However, the event can occur m times not only in

the order indicated in (*), but in many other ways, whose total number is calculated in (5.5). Hence, the probability of the event under consideration occurring m times in a sequence of n trials is equal to

$$\mathcal{P}_n(m) = \frac{n!}{m!(n-m)!} p^m (1-p)^{n-m}. \quad (5.15b)$$

In formula (5.15a), a "trial" means fixing the position of $\equiv$ particle. The result of the trial is that either the particle is in the volume V_1 (probability $p = V_1/V$), or is not in it. The total number of trials is equal to the total number of particles whose position in space has been determined.

The arguments that led to formula (5.15b) can be generalized to the case of several independent events $A_1, A_2, \dots$, having probabilities $p_1, p_2, \dots$ in an individual trial. Since the events are independent, $p_1 + p_2 + \dots = 1$. The probability of a certain sequence of events $A_{i_1}, A_{i_2}, A_{i_3}, \dots$ in a certain series of n trials is equal to $p_{i_1}, p_{i_2}, p_{i_3}, \dots$. The probability of the event A_1 occurring m_1 times, event $A_2 - m_2$ times, and so on, in this sequence of events is

$$\mathcal{P}_n(m_1, m_2, \dots) = \frac{n!}{m_1! m_2! \dots} p_1^{m_1} p_2^{m_2} \dots;$$

$$(m_1 + m_2 + \dots = n), \quad (5.15c)$$

where the factor $n!/(m_1! m_2! \dots)$ takes into account the number of ways in which m_1 events A_1, m_2 events A_2 , etc. can be arranged in the sequence of events. The quantity $\mathcal{P}_n(m_1, m_2, \dots)$ is the probability that the independent event A_1 occurs m_1 times in a series of n trials, and so on.

The binomial distribution (5.15b) is a special case of formula (5.15c). Here, the event under consideration can either occur with a probability $p_1 = p$, or not occur with a probability $p_2 = 1 - p$. Hence, the probability of this event occurring m times in a series of n trials (and hence not occurring $n - m$ times) is given, according to formula (5.15c), by

$$\mathcal{P}_n(m, n-m) = \frac{n!}{m!(n-m)!} p^m (1-p)^{n-m},$$

which coincides with (5.15b).

THE MOST PROBABLE NUMBER OF PARTICLES. It can be directly seen that for very small $m \rightarrow 0$ and for very large

The number of microscopic states used for accomplishing a certain macroscopic state is called the thermodynamic probability of $\equiv$ macroscopic state. This number is very large. The probability of $\equiv$ macroscopic state of $\equiv$ system is the ratio of its thermodynamic probability to the total number of possible microscopic states of the system. The most likely state of an isolated system on its own is its equilibrium state.

$m \rightarrow n$, the value of $\mathcal{P}(V_1, m)$ is very small:

$$\mathcal{P}(V_1, m \rightarrow 0) \simeq q^n \rightarrow 0, \quad \mathcal{P}(V_1, m \rightarrow n) \simeq p^n \rightarrow 0.$$

This is so because q and p are less than unity and n is large. For a certain intermediate value of m , $\mathcal{P}(V_1, m)$ attains its maximum value. In order to find this maximum, we must solve the equation $d\mathcal{P}(V_1, m)/dm = 0$.

Let us calculate this derivative for the case when V_1 and p are small, while q is close to unity. On the other hand, the volume V_1 must not be too small, otherwise p will become negligibly small. In this case, the term p^m will be so small that the multiplier containing factorials in formula (5.15a) is no longer of any importance. Under these conditions, the maximum is attained for quite large values of m and the factorials in (5.15a and b) can be transformed according to Stirling's formula (5.11), although it is not always possible to neglect m in comparison with n . This gives

$$\frac{n!}{m!(n-m)!} \simeq \frac{(n/e)^m}{(m/e)^m [(n-m)/e]^{n-m}} \simeq \left(\frac{n}{m}\right)^m \frac{(1-m/n)^m}{(1-m/n)^n}. \quad (5.16)$$

Since $n \rightarrow \infty$, $(1-m/n)^n = e^{-m}$. Hence, formula (5.15a) assumes the form

$$\mathcal{P}(V_1, m) \simeq \left(\frac{ne}{m}\right)^m p^m q^{n-m} = \left(\frac{nep}{mq}\right)^m q^n. \quad (5.17)$$

Differentiating this expression with respect to m and putting the derivative equal to zero, we obtain an equation for determining the value m_0 for which the maximum is attained:

$$\ln \frac{nep}{m_0 q} - 1 = 0, \quad (5.18)$$

$$m_0 \simeq np/q \simeq np, \quad (5.19)$$

since $q \simeq 1$.

Since all the calculations were made approximately, the relation (5.19) can be considered as an approximate equality. More accurate estimates show that this relation is satisfied with a remarkable degree of accuracy for a large number n of particles in the volume V when the volume V_1 is not too small. The meaning of this result is extremely simple: $n/V = n_0$ is the concentration of particles in the volume V , as if they were distributed uniformly over the entire volume. On the other hand, $n_{\max} = m_0/V_1$ is obviously the most probable



Fig. 7. Binomial distribution for large values of n and $\langle m \rangle$

concentration in volume V_1 . Considering that $p = V_1/V$, we can express equality (5.19) in the following form:

$$n_{\max} = n_0, \quad (5.20)$$

i.e. the most probable concentration of particles in volume V_1 corresponds to a uniform distribution of particles over the entire volume. Since the location of the volume V_1 is quite arbitrary and may be chosen in any part of the volume V , it can be easily concluded that the most probable distribution of the particle density in any volume is a uniform distribution. Such a state of a system is called the stationary equilibrium state (by definition). Hence, the result so obtained can be expressed as follows: the equilibrium state of a system is its most probable state.

THE BINOMIAL DISTRIBUTION. Formula (5.15a) is called the binomial distribution on account of its analogy with Newton's binomial theorem which has the form

$$(q + p)^n = q^n + \frac{n}{1!} p q^{n-1} + \frac{n(n-1)}{2!} p^2 q^{n-2} + \dots + \frac{n(n-1)\dots[n-(m-1)]}{m!} p^m q^{n-m} + \dots + p^n. \quad (5.21)$$

If we take (5.5) into consideration, it becomes obvious that the probabilities (5.15a) coincide with certain terms of the binomial (5.21) if p and q are interpreted as probabilities. In this case, $p + q = 1$, and formula (5.21) is transformed into the probability normalization condition:

$$\sum_{m=0}^n \mathcal{P}(V_1, m) = 1.$$

The dependence of $\mathcal{P}(V_1, m)$ on m is shown in Fig. 7 as a solid curve, since the values of m are very large in the scale that can be practically employed, and hence the points on the curve merge into a continuous curve. This, however, is a characteristic result of graph-plotting and not the possibility of passing a continuous curve through a set of points. The curve is a sharp and narrow peak having its maximum at $m_{\max} = n/V$. The height and width of the peak are connected through the normalization condition

$$\Delta m \mathcal{P}(V_1, m_{\max}) \simeq 1, \quad (5.22)$$

where Δm is the peak width.

Thus, the probability that the number of particles in the volume V_1 will deviate from $m_{\max}$ even insignificantly is negligibly small and falls off rapidly with increasing deviation. However, the number of particles is not always exactly equal to $m_{\max}$ but oscillates around this value. These deviations are called **fluctuations**.

LIMITING FORMS OF THE BINOMIAL DISTRIBUTION. If the number of trials $n \rightarrow \infty$, the distribution (5.15b) tends to a limiting form which depends on the conditions under which n tends to infinity.

There are two important limiting cases:

(1) if $n \rightarrow \infty$ at $p = \text{const}$, we obtain the normal distribution (see Sec. 8);

(2) if $n \rightarrow \infty$ at $np = \text{const}$, we obtain the Poisson distribution.

THE POISSON DISTRIBUTION. Let $\langle m \rangle$ denote the average number of particles in the volume V_1 considered for the derivation of formula (5.15a). Since n/V is the average concentration of particles over the entire volume, $\langle m \rangle/V_1 = n/V$, or $V_1/V = \langle m \rangle/n$. Substituting this value for $V_1/V = p = \langle m \rangle/n$ into (5.15a), we get

$$\mathcal{P}_n(m) = \frac{n!}{m!(n-m)!} \left(\frac{\langle m \rangle}{n} \right)^m \left(1 - \frac{\langle m \rangle}{n} \right)^{n-m}.$$

The right-hand side can be transformed as follows:

$$\begin{aligned} \mathcal{P}_n(m) &= \frac{n(n-1)\dots(n-m+1)}{m!} \frac{(\langle m \rangle)^m}{n^m} \left(1 - \frac{\langle m \rangle}{n} \right)^{n-m} \\ &= 1 \left(1 - \frac{1}{n} \right) \left(1 - \frac{2}{n} \right) \dots \left(1 - \frac{m-1}{n} \right) \frac{(\langle m \rangle)^m}{m!} \frac{(1 - \langle m \rangle/n)^n}{(1 - \langle m \rangle/n)^m}. \end{aligned}$$

This leads to the limiting form of the binomial distribution for $n \rightarrow \infty$:

$$\mathcal{P}(m) = \lim_{n \rightarrow \infty} \mathcal{P}_n(m) = \frac{(\langle m \rangle)^m}{m!} e^{-\langle m \rangle}, \quad (5.23)$$

where the well-known limit $\lim_{n \rightarrow \infty} \left(1 - \frac{\alpha}{n} \right)^n = e^{-\alpha}$ has been used.

Formula (5.23) is called the Poisson distribution. The meaning of this distribution becomes clear during its derivation: if $\langle m \rangle$ events are observed on the average in a certain volume, time interval, etc., the probability of observing m events is equal to $\mathcal{P}(m)$.

Obviously, this formula can be applied for calculating the number of particles in the volume V_1 , if it is known that the average number of particles in this volume is equal to $\langle m \rangle$. By way of another example, we can consider the flow of a gas from a thin-walled vessel through a small hole. In order to ensure that the escape of individual molecules is independent of the fate of other molecules, we shall assume that there is vacuum outside the vessel while inside the vessel the gas is in a rarefied state and the collisions between molecules are rare. In any case, there are no collisions between molecules as they escape through the hole. Besides, in order to ensure that the conditions in the vessel remain unaltered as the molecules escape through the hole, we shall assume that the volume of the vessel and the number of molecules in it are quite large, while the size of the hole and the number of molecules escaping through it during the experiment are quite small.

Clearly, the number of molecules escaping through the hole is proportional to the time interval. Let us count the number of molecules escaping through the hole over an interval Δt . Having conducted a large number of experiments, we can find the mean value, which is proportional to Δt , i.e. has the form $\mu \Delta t$ where μ depends on the experimental conditions. One can ask: "What is the probability that m molecules will be observed in the time interval Δt in the course of an experiment?" This probability is given by the Poisson distribution:

$$\mathcal{P}(m) = \frac{(\mu \Delta t)^m}{m!} e^{-\mu \Delta t}. \quad (5.24)$$

The normalization condition for the Poisson distribution is satisfied in view of the obvious equality

$$\sum_{m=0}^{\infty} \frac{\langle m \rangle^m}{m!} = e^{\langle m \rangle}.$$

It is also worthwhile to note that for large values of $\langle m \rangle = m$, we have

$$\mathcal{P}(m) = \frac{m^m}{m!} e^{-m} \approx \left(\frac{e}{m}\right)^m \left(\frac{m}{e}\right)^m \approx 1,$$

where Stirling's formula $m! \approx (m/e)^m$ has been used. This means that the probability $\mathcal{P}(m \neq \langle m \rangle) \approx 0$ for large m , and

the distribution of probabilities near $m = \langle m \rangle$ rapidly falls from its peak value for $m = \langle m \rangle$ as shown in Fig. 7.

Example 5.1. There are 10 white balls and 5 black balls in an urn. Five draws are made from the urn, and the ball is returned to the urn each time after the draw. Find the probability of drawing three white balls and two black balls in this experiment.

This is a typical example in which the distribution (5.15c) is applicable. We have

$$\mathcal{P}_5(3, 2) = \frac{5!}{3! 2!} \left(\frac{10}{15}\right)^3 \left(\frac{5}{15}\right)^2 = 10 \left(\frac{2}{3}\right)^3 \left(\frac{1}{3}\right)^2 \simeq 0.329.$$

Example 5.2. Long-term observations at one of the metro stations revealed that between 8:45 and 8:50 a.m. on a certain day of the week, 70% of the passengers pass the turnstiles, by paying through the slot-machine, 20% use season tickets, while 10% buy their tickets at the window. What is the probability that out of 10 randomly selected passengers, 7 will use the turnstiles, 2 will produce season tickets, and one passenger will buy his ticket at the window?

Since these three alternatives constitute the complete system of possibilities for each passenger, we get

$$\mathcal{P}_{10}(7, 2, 1) = \frac{10!}{7! 2! 1!} \left(\frac{7}{10}\right)^7 \left(\frac{2}{10}\right)^2 \left(\frac{1}{10}\right)^1 = 0.0800.$$

Example 5.3. The analysis of a typist's work showed that on 20% working days in the year she made less than four mistakes, on 50% of the days the number of mistakes was between 5 and 10, while on the remaining 30% days, the number of mistakes exceeded 10. What is the probability that she will make more than ten mistakes on three days out of five?

The probability of her making less than four mistakes, from five to ten mistakes, and more than ten mistakes on a certain day is $p_1 = 0.2$, $p_2 = 0.5$, and $p_3 = 0.3$ respectively.

The typist can make more than ten mistakes on three days in the following three cases:

(1) the number of mistakes on the remaining two days is less than four:

$$\mathcal{P}_5(2, 0, 3) = \frac{5!}{2! 3!} (0.2)^2 (0.3)^3.$$

Here, the argument of the probability $\mathcal{P}_5$ shows the number of days when the mistakes correspond to the probabilities p_1 , p_2 , and p_3 respectively,

(2) the number of mistakes on the remaining two days is

between 5 and 10:

$$\mathcal{P}_5(0, 2, 3) = \frac{5!}{2!3!} (0.5)^2 (0.3)^3;$$

(3) the number of mistakes on one day is less than four, and between five and ten on the other days:

$$\mathcal{P}_5(1, 1, 3) = \frac{5!}{3!} 0.2 \cdot 0.5 \cdot (0.3)^3.$$

These three cases exhaust all the possibilities under which the typist can make more than ten mistakes on three days out of five. The total probability that there will be three days in a week of five when the typist will make more than ten mistakes on each day is equal to the sum of the individual probabilities:

$$\begin{aligned} \mathcal{P} &= \mathcal{P}_5(2, 0, 3) + \mathcal{P}_5(0, 2, 3) + \mathcal{P}_5(1, 1, 3) \\ &= \frac{5!}{2!3!} (0.3)^3 [(0.2)^2 + (0.5)^2 + 2 \cdot 0.2 \cdot 0.5] = 0.132. \end{aligned}$$

In other words, there will be just 13% weeks when the typist will make more than ten mistakes on three days.

Sec. 6. FLUCTUATIONS

The fluctuations of physical quantities are considered by taking as an example the number of particles in a volume. The fluctuations are calculated on the basis of the binomial distribution. A general conclusion is drawn about the dependence of the relative fluctuation on the number of particles in the system.

AVERAGE NUMBER OF PARTICLES IN A VOLUME. In accordance with the above arguments, it can be concluded that the number of particles in a certain volume does not remain constant in time, but changes continuously in a small interval. In principle, large deviations are also possible, but their probability is low and hence they are encountered extremely rarely. The time dependence of the number of particles in a volume V_1 is shown in Fig. 8. By definition, the average number of particles in the volume V_1 is equal to

$$\langle m \rangle_t = \frac{1}{T} \int_{t_0}^{t_0+T} m(t) dt \quad (6.1)$$

as $T \rightarrow \infty$. The dependence of m on t is not known, and hence it is impossible to calculate the mean. However, we can reduce the time average to the ensemble average with the help of the ergodic hypothesis and use formula (4.5).

This gives

$$\langle m \rangle_t = \langle m \rangle_a = \sum_{m=0}^n m \mathcal{P}(V_1, m) = \sum_{m=0}^n \frac{n!}{m!(n-m)!} p^m q^{n-m}. \quad (6.2)$$

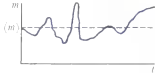


Fig. 8. Fluctuations of the number of particles

This quantity can be calculated easily in the following way:

$$\begin{aligned} \sum_{m=0}^n \frac{mn!}{m!(n-m)!} p^m q^{n-m} &= p \frac{\partial}{\partial p} \sum \frac{n!}{m!(n-m)!} p^m q^{n-m} \\ &= p \frac{\partial}{\partial p} (p+q)^n = pn(p+q)^{n-1}. \end{aligned} \quad (6.3)$$

Since $p+q=1$, we get

$$\langle m \rangle_t = \langle m \rangle_a = pn. \quad (6.4)$$

This means that the average density in the volume V_1 is equal to the average density over the entire volume V . Since we are using the ergodic hypothesis, we shall not be indicating in future the volume over which the averaging is being made.

FLUCTUATIONS. The measure of fluctuations is the standard deviation from the mean, defined by Eq. (2.19). While calculating this quantity, we can replace the time averaging by ensemble averaging. Formula (2.19) shows that in order to find the standard deviation, we must calculate $\langle m^2 \rangle$ in addition to $\langle m \rangle$:

$$\langle m^2 \rangle = \sum_{m=0}^n \frac{n!}{m!(n-m)!} \frac{m^2}{m!} p^m q^{n-m}. \quad (6.5)$$

We use the same method that was employed for calculating (6.3):

$$\begin{aligned} \sum_{m=0}^n \frac{n!}{m!(n-m)!} \frac{m^2}{m!} p^m q^{n-m} &= p \frac{\partial}{\partial p} p \frac{\partial}{\partial p} \sum \frac{n!}{m!(n-m)!} p^m q^{n-m} \\ &= p \frac{\partial}{\partial p} p \frac{\partial}{\partial p} (p+q)^n = p \left[n(p+q)^{n-1} + pn(n-1)(p+q)^{n-2} \right]. \end{aligned} \quad (6.6)$$

Considering that $p+q=1$, we obtain

$$\langle m^2 \rangle_a = npq + n^2 p^2. \quad (6.7)$$

Hence, with the help of the dispersion relation (2.26), we get

$$\langle (\Delta m)^2 \rangle = \langle m^2 \rangle - \langle m \rangle^2 = npq. \quad (6.8)$$

Consequently, the standard deviation is equal to

$$\sigma = \sqrt{\langle (\Delta m)^2 \rangle} = \sqrt{npq}. \quad (6.9)$$

This equality shows that the standard deviation increases more slowly than the total number of particles in a system, while the mean deviation (6.4) increases in proportion to the number of particles in the system. This means that the relative standard deviation decreases with increasing number of particles in the system:

$$\frac{\sqrt{\langle(\Delta m)^2\rangle}}{\langle m \rangle} = \sqrt{\frac{q}{p}} \frac{1}{\sqrt{n}}. \quad (6.10)$$

The physical meaning of this relation is extremely important. For the case under consideration, we can write formula (6.10) in the following form:

$$\frac{\sqrt{\langle(\Delta m)^2\rangle}}{\langle m \rangle} = \sqrt{\frac{V}{V_1} - 1} \frac{1}{\sqrt{n}}. \quad (6.11)$$

As $V_1 \rightarrow V$, the relative value of fluctuations tends to zero, and vanishes for $V_1 = V$, since the total number of particles over the entire volume is fixed and equal to n and there are no fluctuations of this number. With decreasing V_1 , the relative value of fluctuations increases. For $V_1 \ll V$, we can neglect unity in comparison with $(V/V_1) \gg 1$ in (6.11) and write this formula in the following form:

$$\frac{\sqrt{\langle(\Delta m)^2\rangle}}{\langle m \rangle} = \sqrt{\frac{V}{V_1}} \frac{1}{\sqrt{n}} = \frac{1}{\sqrt{\langle m \rangle}}, \quad (6.12)$$

where $n = \langle m \rangle V/V_1$. It can be seen from (6.12) that the relative role of fluctuations increases with a decrease in the volume in which these fluctuations are considered. For example, if we consider a volume containing only a few particles on the average, the relative value of fluctuations constitutes a considerable fraction of the number of particles. If the volume is so small that it contains only ten particles on the average, the relative standard deviation is about 1/3. If, on the other hand, we consider a volume $1 \text{ mm}^3 = 10^{-3} \text{ cm}^3$ under normal atmospheric conditions, it will contain an average number $\langle m \rangle = 2.7 \times 10^{16}$ particles, and the relative standard deviation will be less than 10^{-8} , which is a very small value. Hence, the statistical fluctuations are insignificant in macroscopic systems. It can be stated to a great degree of accuracy that the quantities are equal to their mean values.

Let us calculate the relative value of fluctuations with the

! A system in an equilibrium state continues to undergo constant changes by going over from one microscopic state into another. Since it "is not capable" of preferring one microscopic state over another, the transitions of the system may or may not disturb the equilibrium state. However, the system cannot go very far from the equilibrium state, since in this case the chaotic transitions of the system from one microscopic state to another lead to an ordered motion towards the equilibrium state. Consequently, the system moves in the neighbourhood of the equilibrium state, i.e. fluctuates.

help of Poisson's distribution:

$$\begin{aligned}
 \langle m^2 \rangle &= \sum_{m=0}^{\infty} \frac{m^2 (\langle m \rangle)^m}{m!} e^{-\langle m \rangle} \\
 &= \sum_{m=0}^{\infty} \frac{[m(m-1) + m] (\langle m \rangle)^m}{m!} e^{-\langle m \rangle} \\
 &= \sum_{m=2}^{\infty} \frac{(\langle m \rangle)^m}{(m-2)!} e^{-\langle m \rangle} + \sum_{m=1}^{\infty} \frac{(\langle m \rangle)^m}{(m-1)!} e^{-\langle m \rangle} \\
 &= \langle m \rangle^2 + \langle m \rangle.
 \end{aligned}$$

Consequently, $\langle (\Delta m)^2 \rangle = \langle m^2 \rangle - (\langle m \rangle)^2 = \langle m \rangle$, and

$$\frac{\sqrt{\langle (\Delta m)^2 \rangle}}{\langle m \rangle} = \frac{1}{\sqrt{\langle m \rangle}}.$$

As expected, this expression is identical with (6.12).

All the above discussion concerning fluctuations in a system of an ideal gas is of a general nature and is also applicable to all the other systems as well. This is evident from the fact that only the general statistical properties of a system have been used in the derivation of all the relations, and no special relations have been used which are applicable only to the system under consideration. However, it is advisable to consider this question for the general case as well.

RELATIVE VALUE OF FLUCTUATIONS. Suppose that a system of n particles is characterized by a quantity F which is the sum of the corresponding quantities for the particles of the system:

$$F = \sum_{i=1}^n f_i, \quad (6.13)$$

where f_i is the value of f for the i -th particle. For example, if F is the kinetic energy of all the particles of the system, f_i is the kinetic energy of the i -th particle.

The mean value of quantities appearing in formula (6.13) may be calculated over time or over the ensemble. According to the ergodic hypothesis, the result will be the same in both cases. Hence we shall denote the averaging by the usual symbol $\langle \rangle$, but shall not indicate the variable over which the



The relative role of fluctuations decreases with increasing volume and the average number of particles in it. Hence the statistical fluctuations in macroscopic systems are insignificant and all quantities can be taken equal to their mean values with a high degree of accuracy.

averaging is carried out. From (6.13) it follows that

$$\langle F \rangle = \sum_{i=1}^n \langle f_i \rangle. \quad (6.14)$$

It should be noted that in this case $\langle F \rangle$ is not the sum of the energies of all the particles of a system at a certain instant of time, divided by the total number of particles. This quantity is either the time average of the total kinetic energy of all particles of the given system, or the ensemble average of the system of particles (the number of particles in the system is $N \rightarrow \infty$). The same is true for $\langle f_i \rangle$.

Since all the particles in the system are identical, the mean value $\langle f_i \rangle$ will be the same for all particles:

$$\langle f_i \rangle = \langle f_j \rangle = \dots = \langle f \rangle. \quad (6.15)$$

Hence, we can write (6.14) in the form

$$\langle F \rangle = n \langle f \rangle. \quad (6.16)$$

Let us calculate the root-mean-square deviation of F from the mean value $\langle F \rangle$. By definition,

$$\Delta F = F - \langle F \rangle = \sum_{i=1}^n (f_i - \langle f \rangle) = \sum_{i=1}^n \Delta f_i. \quad (6.17)$$

Squaring both sides of this equation and averaging the expressions thus obtained, we get

$$\langle (\Delta F)^2 \rangle = \left\langle \sum_{i,j=1}^n \Delta f_i \Delta f_j \right\rangle = \sum_{i=1}^n \langle (\Delta f_i)^2 \rangle + \sum_{i \neq j} \langle \Delta f_i \Delta f_j \rangle. \quad (6.18)$$

The sum on the right-hand side has been split into two parts. The first sum contains terms with identical indices, while the second sum contains the terms with different indices. Naturally, $\langle \Delta f_i \Delta f_j \rangle = 0$, since the deviations Δf_i and Δf_j , which correspond to different particles, are not related and their averaging gives zero. In the first sum, on the other hand, $\langle (\Delta f_i)^2 \rangle$ is the same for all the particles in view of their identity. Hence, (6.18) assumes the form

$$\langle (\Delta F)^2 \rangle = n \langle (\Delta f)^2 \rangle. \quad (6.19)$$

From (6.16) and (6.19), we get for the relative standard deviation

$$\frac{\sqrt{\langle (\Delta F)^2 \rangle}}{\langle F \rangle} = \frac{\sqrt{\langle (\Delta f)^2 \rangle}}{\langle f \rangle} \frac{1}{\sqrt{n}}.$$

(6.20)

?

1. Why can't the fluctuations be characterized simply by the average value of the deviation from the mean?
2. What general properties of the dependence of the standard deviation and the mean value on the number of particles in a system can be used for explaining the decrease in the relative role of fluctuations with increasing number of particles?

Formula (6.20) proves in the general form, that the relative standard deviation of a quantity pertaining to a system of particles decreases in inverse proportion to the square root of the number of particles in the system and becomes negligibly small if the number of particles is large. Hence the behaviour of a system of a large number of particles can be described with the help of the mean values characterizing the system.

Example 6.1. Gas molecules escape from a very small hole of area $S = 10^{-10} \text{ m}^2$, drilled through the wall of a vessel containing a highly rarefied gas. The hole is so small that the escaping particles do not collide with one another, nor do they violate the state of the gas inside the vessel to any appreciable extent. The mean frequency of impacts of the molecules against the vessel wall is $\nu = 10^{26} \text{ s}^{-1} \cdot \text{m}^{-2}$. Outside the vessel, the number of escaping molecules is measured periodically over time intervals of $\tau = 10^{-2} \text{ s}$ each. Find the relative fluctuation of the molecules escaping during one such time interval.

The average number of molecules escaping during the interval τ is equal to $\langle n \rangle = \nu S \tau$. Hence, the relative fluctuation of the number of escaping molecules is equal to

$$\frac{\sqrt{\langle (\Delta n)^2 \rangle}}{\langle n \rangle} = \frac{1}{\sqrt{\langle n \rangle}} = \frac{1}{\sqrt{\nu S \tau}} = \frac{1}{\sqrt{10^{26} \times 10^{-10} \times 10^{-2}}} = 10^{-7}.$$

Example 6.2. Find the mean value of the product $f_1 f_2$ of two arbitrary physical quantities which fluctuate about their mean values $\langle f_1 \rangle$ and $\langle f_2 \rangle$.

By definition,

$$f_1 = \langle f_1 \rangle + \Delta f_1, \quad f_2 = \langle f_2 \rangle + \Delta f_2.$$

Hence,

$$\begin{aligned} \langle f_1 f_2 \rangle &= \langle \langle f_1 \rangle \langle f_2 \rangle \rangle + \langle \langle f_1 \rangle \Delta f_2 \rangle \\ &\quad + \langle \Delta f_1 \langle f_2 \rangle \rangle + \langle \Delta f_1 \Delta f_2 \rangle \\ &= \langle f_1 \rangle \langle f_2 \rangle + \langle f_1 \rangle \langle \Delta f_2 \rangle + \langle \Delta f_1 \rangle \langle f_2 \rangle + \langle \Delta f_1 \Delta f_2 \rangle \\ &= \langle f_1 \rangle \langle f_2 \rangle + \langle \Delta f_1 \Delta f_2 \rangle, \end{aligned} \quad (6.21)$$

where $\langle \Delta f_1 \rangle = 0$, $\langle \Delta f_2 \rangle = 0$.

The quantities are called statistically independent if $\langle \Delta f_1 \Delta f_2 \rangle = 0$. In this case, formula (6.21) is simplified to the following form:

$$\langle f_1 f_2 \rangle = \langle f_1 \rangle \langle f_2 \rangle. \quad (6.22)$$

Sec. 7. THE CANONICAL ENSEMBLE. GIBBS DISTRIBUTION

The peculiarities of a canonical system are compared with those of a microcanonical system. The Gibbs distribution is introduced. The role of the partition function in the theory is described, and an example has been given to illustrate the use of the partition function for calculating the mean.

THE VELOCITY- AND ENERGY MICROSCOPIC STATES. So far, we have been dealing with a microcanonical ensemble where we could abstain from an analysis of the velocity microscopic states of the particles. This is so because in the equilibrium state, the number of velocity microscopic states of particles is obviously the same and equal to the maximum number of microscopic states compatible with the condition that the total energy remains constant. The ergodic hypothesis and the equal probability postulate were the main concepts that were employed for studying the properties of a microcanonical ensemble.

Now we must investigate the velocity distribution of microscopic states of particles. We pick up a certain particle and observe its velocity in one system of the ensemble at different instants of time, as well as in different systems at the same instant of time. An investigation of the particle velocity also gives a complete picture of its kinetic energy. It is quite clear that the velocity and kinetic energy of a particle vary as a result of collisions with other particles. Thus, a particle in different systems of the ensemble is in different velocity- and energy states. If we observe this particle in one of the systems, its velocity and energy microscopic states will change with time. Our task is to determine these velocity- and energy microscopic states.

DEFINITION OF A CANONICAL ENSEMBLE. Let us consider the velocity and energy microscopic states of a particle, representing the system under consideration. However, this system is no longer closed, since it exchanges energy with other particles which together with this particle form a closed system. The aggregate of closed systems forms a microcanonical ensemble. The aggregate of the corresponding open systems constitutes a canonical ensemble. Thus, an individual system in the canonical ensemble is a part of a large closed system. An individual system of a canonical ensemble is a part of a large system not in the sense that it occupies a part of its space, but in the sense of energy- and velocity states. In the spatial sense, this part may coincide with the entire system. A separate part of a canonical ensemble may contain one or more particles, the only important point being that the number of component particles should be much smaller than the number of particles in the larger system. Different systems of a canonical ensemble have different energies. It is required to find the probabilities of different energy states of the systems

constituting a canonical ensemble. The solution of this problem gives a complete information about all the states in a system of the canonical ensemble, since the aggregate of states with the same energy constitutes a microcanonical ensemble and has already been investigated. An isolated system in a canonical ensemble is called a canonical system.

It follows from the definition of a canonical ensemble that an analysis of energy distribution of systems may involve not only kinetic energy, but potential energy as well.

GIBBS CANONICAL DISTRIBUTION. For the sake of simplicity, we shall call a canonical system a subsystem, while the system whose part this subsystem is will be called a system. It should be emphasized once again that the system belongs to a microcanonical ensemble and its total energy is constant and equal to ϵ_0 . Let ϵ_α be the energy of the subsystem. Then the energy of the remaining part of the system will be equal to $\epsilon_0 - \epsilon_\alpha$. The given state of the subsystem is one of the specific microscopic states. Besides this (microscopic) state, there may, and, indeed, do exist other microscopic states of the subsystem with the same energy ϵ_α . Since the complete system belongs to a microcanonical ensemble, all its states have equal probabilities. Let us denote the number of these states of the complete system by Γ_0 . The probability of each state is equal to $1/\Gamma_0$. The state of the subsystem under consideration is attained through several states of the complete system. We denote the number of these states by Γ_α . Then, the probability $\mathcal{P}_\alpha$ of the subsystem being in the state with energy ϵ_α can be written as follows in accordance with the definition of probability in microcanonical ensembles:

$$\mathcal{P}_\alpha = \Gamma_\alpha / \Gamma_0, \quad (7.1)$$

where $\Gamma_0 = \Gamma_0(\epsilon_0)$ is the total number of microscopic states of the system, and $\Gamma_\alpha(\epsilon_0 - \epsilon_\alpha)$ is the number of microscopic states of the complete system through which we attain the state with the energy ϵ_α of the subsystem.

For practical applications, it is more convenient to use formula (7.1) in a different form. Using the obvious relation $a = \exp \ln a$, we can rewrite this formula as

$$\mathcal{P}_\alpha = \frac{1}{\Gamma_0} e^{\ln \Gamma_\alpha}. \quad (7.2)$$

The energy ϵ_α has a negligibly small value in comparison with ϵ_0 , while the logarithm is a very slowly varying function,



Josiah Willard
Gibbs
(1839-1903)

especially for large arguments. Hence, $\ln \Gamma_\alpha$ can be expanded into a Taylor series at the point ϵ_0 , confining in the expansion to the term linear in ϵ_α :

$$\ln \Gamma_\alpha(\epsilon_0 - \epsilon_\alpha) = \ln \Gamma_\alpha(\epsilon_0) - \epsilon_\alpha \frac{\partial \ln \Gamma_\alpha(\epsilon_0)}{\partial \epsilon_0}, \quad (7.3)$$

where $\Gamma_\alpha(\epsilon_0)$ is the number of microscopic states of the complete system through which we attain the state in which the subsystem has zero energy. Clearly, this number does not depend on ϵ_α , i.e. $\Gamma_\alpha(\epsilon_0) = \Gamma_{\alpha 0}$. Besides, it is quite obvious that the number of microscopic states increases with energy, i.e. $(\partial \ln \Gamma_\alpha / \partial \epsilon_0) > 0$. Hence,

$$\beta = \frac{\partial \ln \Gamma_{\alpha 0}}{\partial \epsilon_0} > 0 \quad (7.4)$$

is a positive constant quantity that does not depend on ϵ_α . Since any small part of the system, or any small part of any subsystem can be chosen as the subsystem, and since according to the above argument β has the same value for all of them, we can conclude that β is a fundamental characteristic of the canonical as well as the microcanonical ensemble containing the complete system under consideration. This fundamental quantity is temperature, which is related to β through a simple relation [see (8.15)].

Taking into account (7.3) and (7.4), we can transform (7.2) as follows:

$$\mathcal{P}_\alpha = A e^{-\beta \epsilon_\alpha}, \quad (7.5)$$

where $A = (1/\Gamma_0) \exp \ln \Gamma_{\alpha 0} = \Gamma_{\alpha 0} / \Gamma_0$ is a constant.

Formula (7.5) is called the Gibbs distribution and provides a solution for the problem formulated above. This formula is also called the canonical distribution. It should be noted once again that $\mathcal{P}_\alpha$ in this formula is the probability of one of the states of the subsystem with energy ϵ_α .

The states of a subsystem with the same energy ϵ_α belong to a microcanonical ensemble and are therefore equally probable. Hence, if their number is equal to g_α , the probability $\mathcal{P}(\epsilon_\alpha)$ of the subsystem being in the state with energy ϵ_α is given, according to the probability addition rule, by the following relation:

$$\mathcal{P}(\epsilon_\alpha) = g_\alpha \mathcal{P}_\alpha = A g_\alpha e^{-\beta \epsilon_\alpha}. \quad (7.6)$$

If the distribution of the energy states is continuous, we can denote the number of microscopic states in the energy interval between ϵ_α and $\epsilon_\alpha + d\epsilon_\alpha$ by

$$dg_\alpha = \rho(\epsilon_\alpha) d\epsilon_\alpha \quad (7.7)$$

and write

$$d\mathcal{P}(\epsilon_\alpha) = A e^{-\beta\epsilon_\alpha} \rho(\epsilon_\alpha) d\epsilon_\alpha, \quad (7.8)$$

where $d\mathcal{P}(\epsilon_\alpha)$ is the probability that the subsystem is in one of the states with energy between ϵ_α and $\epsilon_\alpha + d\epsilon_\alpha$. The density

$$p_\rho(\epsilon_\alpha) = d\mathcal{P}(\epsilon_\alpha)/d\epsilon_\alpha \quad (7.9)$$

is called the probability density for the subsystem having the energy ϵ_α . Taking into account Eq. (7.8), we can write

$$p_\rho(\epsilon_\alpha) = A e^{-\beta\epsilon_\alpha} \rho(\epsilon_\alpha). \quad (7.10)$$

The constant A is found from the normalization condition, while the constant β is related with the temperature.

NORMALIZATION OF DISTRIBUTION. For the sake of simplicity of analysis, it is more convenient to use the concept of discrete distribution over different states. Let us use the index α in formula (7.5) to mark different states, including those belonging to the same energy level. All possible states of the system form a complete set of possible states. Hence the normalization condition must be satisfied:

$$\sum_{\alpha} \mathcal{P}_{\alpha} = 1. \quad (7.11)$$

From this, we can calculate the constant

$$A = 1 / \sum_{\alpha} e^{-\beta\epsilon_{\alpha}}. \quad (7.12)$$

Consequently, the canonical distribution has the form

$$\mathcal{P}_{\alpha} = e^{-\beta\epsilon_{\alpha}} / \sum_{\alpha} e^{-\beta\epsilon_{\alpha}}. \quad (7.13)$$

CALCULATION OF THE MEAN VALUES. Let f be a certain quantity having the value f_{α} in the state α . Its mean value is equal to

$$\langle f \rangle = \sum_{\alpha} f_{\alpha} e^{-\beta\epsilon_{\alpha}} / \sum_{\alpha} e^{-\beta\epsilon_{\alpha}}. \quad (7.14)$$

PARTITION FUNCTION. Of special importance is the mean value of the energy of the system:

$$\langle \epsilon \rangle = \frac{\sum_{\alpha} \epsilon_{\alpha} e^{-\beta \epsilon_{\alpha}}}{\sum_{\alpha} e^{-\beta \epsilon_{\alpha}}} = -\partial \ln Z / \partial \beta, \quad (7.15)$$

where

$$Z = \sum_{\alpha} e^{-\beta \epsilon_{\alpha}} \quad (7.16)$$

is called the **partition function**. It plays a very important role, since it can be used for expressing many important quantities in statistical physics. An example for calculating (7.16) is considered in Sec. 12.

FLUCTUATIONS. These can be easily calculated in a canonical system with the help of formula (7.14) for the mean value. The dependence of fluctuations on the size of a system in the general case was described in Sec. 6.

Example 7.1. Find the root-mean-square deviation of energy from its mean value with the help of the partition function. Also find the relative value of fluctuations.

Proceeding in the same way as Eq. (7.15), we obtain

$$\langle \epsilon^2 \rangle = \left[\sum_{\alpha} \epsilon_{\alpha}^2 e^{-\beta \epsilon_{\alpha}} \right] / \left[\sum_{\alpha} e^{-\beta \epsilon_{\alpha}} \right] = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}.$$

Next, we get

$$\begin{aligned} \langle (\epsilon - \langle \epsilon \rangle)^2 \rangle &= \langle \epsilon^2 \rangle - (\langle \epsilon \rangle)^2 = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right)^2 \\ &= \frac{\partial}{\partial \beta} \left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) = - \frac{\partial \langle \epsilon \rangle}{\partial \beta}. \end{aligned}$$

Considering that the energy of the system is proportional to the total number of particles, i.e. $\epsilon \propto n$, we find

$$\left[\frac{\langle (\epsilon - \langle \epsilon \rangle)^2 \rangle}{\epsilon^2} \right]^{1/2} = \left| \frac{\partial \langle \epsilon \rangle}{\epsilon^2 \partial \beta} \right|^{1/2} \propto \left(\frac{n}{n^2} \right)^{1/2} = \frac{1}{\sqrt{n}}.$$

! Partition function is a very important characteristic of a system. Since it is the result of summation over all microscopic states, it is not a function of any one of them, but is rather a function of all these states simultaneously, i.e. a function of parameters characterizing the macroscopic state. Thus the partition function allows us to express the parameters describing the macroscopic state of a system in terms of quantities characterizing its microscopic state.

Sec. 8. MAXWELL DISTRIBUTION

Two possible approaches are indicated for studying the distribution of particles in a system. The density of states is discussed. The main peculiarities of the Maxwell distribution and its relation to the Gauss distribution are considered. The derivation and the applicability conditions of the Gauss distribution are considered. The experimental verification of the Maxwell distribution is described. The detailed balancing principle is discussed.

TWO APPROACHES TO STUDYING PARTICLE DISTRIBUTION. Let us consider a velocity (and energy) distribution of particles of an ideal gas. We can proceed in two ways. We can take the entire system of n particles as a canonical system which is a part of a large microcanonical system. But a system of n particles can also be treated as an aggregate of independent canonical systems each of which contains one particle. Such a canonical ensemble was used in Sec. 7 for analyzing the main concepts associated with canonical ensembles. Calculations using the first method involve cumbersome combinatorial methods similar to those used in Sec. 5. Here, we shall use the second approach in which the calculations are made directly on the basis of the probability theory relations and do not involve cumbersome calculations.

DENSITY OF STATES. We start with formula (7.5) in which $\mathcal{P}_\alpha$ for a single particle means the probability of its being located in one of the states with energy ε_α . As has already been mentioned in connection with formula (4.1), one particle occupies a volume $(2\pi\hbar)^3$ in the coordinate-momentum (phase) space. Then, the number of states of one particle contained in a phase volume $dx dy dz dp_x dp_y dp_z$ will be equal to

$$d\Gamma = dx dy dz dp_x dp_y dp_z / (2\pi\hbar)^3. \quad (8.1)$$

Consequently, in analogy with (7.6) we get the following relation for the probability of finding a particle in the phase volume:

$$d\mathcal{P} = A e^{-\beta\varepsilon_\alpha} d\Gamma. \quad (8.2)$$

In order to go over to the probability that the particle has the energy ε_α , we must integrate (8.2) with respect to all the elements of the phase volume corresponding to ε_α . In the present case, the energy ε of the particle does not depend on the coordinates, and hence integration over $dx dy dz$ gives the volume V in which the particle is located. For integration over $dp_x dp_y dp_z$, we must consider that the energy of the particle is

$$\begin{aligned} \varepsilon &= \frac{mv^2}{2} = \frac{mv_x^2}{2} + \frac{mv_y^2}{2} + \frac{mv_z^2}{2} \\ &= \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} = \frac{p^2}{2m}, \end{aligned} \quad (8.3)$$

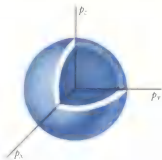


Fig. 9. System of coordinates in the momentum space

where $p_x = mv_x$, etc. The surface of constant-energy states in the momentum space is the sphere $p^2 = \text{const}$ (Fig. 9). Integration over a spherical layer of thickness dp at the surface corresponding to the energy $\varepsilon = p^2/(2m)$ is equivalent to the substitution $dp_x dp_y dp_z = 4\pi p^2 dp$. Hence, we can write instead of (8.1)

$$d\Gamma = \frac{V4\pi p^2 dp}{(2\pi\hbar)^3} = \frac{V4\pi m^3 v^2 dv}{(2\pi\hbar)^3}, \quad (8.4)$$

where $v = p/m$ is the varying velocity which is used as an independent variable in the analysis of gases. Similarly, expressing the energy in terms of the velocity through the formula $\varepsilon = mv^2/2$, we can finally express (8.2) in the form

$$d\mathcal{P}(v) = A \frac{V4\pi m^3}{(2\pi\hbar)^3} e^{-\beta mv^2/2} v^2 dv, \quad (8.5)$$

where $d\mathcal{P}(v)$ is the probability that the magnitude of the velocity lies between v and $v + dv$. The constant A is found from the normalization condition

$$\int_{v=0}^{\infty} d\mathcal{P}(v) = 1. \quad (8.6)$$

The problem is thus reduced to the computation of

$$\int_0^{\infty} e^{-\beta mv^2/2} v^2 dv = \left(\frac{2}{\beta m}\right)^{3/2} \int_0^{\infty} e^{-\xi^2} \xi^2 d\xi = \left(\frac{2}{\beta m}\right)^{3/2} \frac{\sqrt{\pi}}{4}, \quad (8.7)$$

where

$$\int_0^{\infty} e^{-\beta \xi^2} d\xi = \frac{\sqrt{\pi}}{2} \frac{1}{\sqrt{\beta}}. \quad (8.8)$$

Differentiation of (8.8) with respect to parameter β leads to the formula

$$\int_0^{\infty} e^{-\beta \xi^2} \xi^2 d\xi = \frac{\sqrt{\pi}}{4} \frac{1}{\beta^{3/2}}, \quad (8.9)$$

which was used while calculating the integral (8.7). Taking (8.7) into account, we obtain from the condition (8.6)

$$A \frac{V4\pi m^3}{(2\pi\hbar)^3} \left(\frac{2}{\beta m}\right)^{3/2} \frac{\sqrt{\pi}}{4} = 1. \quad (8.10)$$

From this we can find A . Substituting the expression obtained in this way into (8.5), we obtain the following final

!

The energy of molecules changes as a result of collisions. For a specific molecule, the probability of gaining or losing energy as a result of collisions is not the same and depends on the ratio of the molecular energy and the most probable energy of gas molecules. If the energy of the molecule is less than the most probable energy, it is more likely to gain energy with a passage of time as a result of collisions. However, the molecule can also lose energy. If the molecule has the energy higher than the most probable energy, there is a greater likelihood of its

expression for the required probability:

$$d\mathcal{P}(v) = \frac{4}{\sqrt{\pi}} \left(\frac{\beta m}{2} \right)^{3/2} e^{-\beta m v^2/2} v^2 dv. \quad (8.11)$$

MAXWELL DISTRIBUTION. In order to apply (8.11) to a system of n particles, we must use the probability summation rule, treating each particle of the system as independently and randomly moving (which is in complete accord with the nature of motion of particles of an ideal gas). The number of particles whose velocities lie between v and $v + dv$ is

$$dn(v) = n d\mathcal{P}(v). \quad (8.12)$$

Consequently, the relative number of particles with velocities in the interval $(v, v + dv)$ will be

$$\frac{dn(v)}{n} = d\mathcal{P}(v) = \frac{4}{\sqrt{\pi}} \left(\frac{\beta m}{2} \right)^{3/2} e^{-\beta m v^2/2} v^2 dv. \quad (8.13)$$

losing energy with the passage of time as a result of collisions. However, the possibility of its acquiring energy cannot be ruled out either. Hence, in some respect, a universal justice ultimately "triumphs" in a system of molecules: molecules with a low energy gain energy on the average, while those with a high energy lose it. Over a sufficiently long interval of time, each individual molecule "possesses" low as well as high values of energy. The average energies of all molecules are identical and equal to the mean energy of all molecules at any instant of time (ergodic hypothesis). However, at any given moment of time, the energies of molecules are not equal, and that is where the Maxwell distribution comes into play.

This formula is called the Maxwell distribution. It characterizes the velocity distribution of gas particles in the equilibrium state.

Before going over to the analysis of this formula, we must find out the meaning of the parameter β .

The law (8.13) of the velocity distribution of gas molecules was first obtained by Maxwell in 1860. A more rigorous proof was given in 1866.

The quantity $d\mathcal{P}(v)/dv$ is the density of the probability that the particles have a velocity v , where we are talking about magnitude of the velocity. It can be seen from (8.13) that the distribution of molecular velocities in all directions is isotropic and all the directions are equally probable for velocities.

TEMPERATURE. Let us calculate the mean kinetic energy of particles:

$$\left\langle \frac{mv^2}{2} \right\rangle = \int_0^\infty \frac{mv^2}{2} d\mathcal{P}(v) = \frac{3}{2} \frac{1}{\beta}, \quad (8.14)$$

where the integral is evaluated with the help of formula (8.9) after differentiation with respect to the parameter β . Thus, β characterizes an extremely important quantity describing



James Clerk
Maxwell
(1831-1879)

a statistical system, viz. the mean kinetic energy of the particles of the system. The reciprocal of β is called the temperature:

$$1/\beta = kT, \quad (8.15)$$

where k is the proportionality factor called the Boltzmann constant.

If we take into account (8.15), the Maxwell distribution (8.13) assumes the form

$$dn/n = d\mathcal{P}(v) = f(v) dv,$$

$$f(v) = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-mv^2/(2kT)} v^2. \quad (8.16)$$

The temperature T is introduced through formula (8.15) purely formally and by way of a definition. It is called the thermodynamic temperature (see Secs. 11 and 21). For the time being, it is sufficient to know this without proof and to intuitively use the concept of temperature which everybody is familiar with. In the SI system, the unit of temperature is a kelvin. It is connected to the temperature $t^\circ\text{C}$ on the Celsius scale through the relation $T = t + 273.15$. The Boltzmann constant $k = 1.380662 \times 10^{-23}$ J/K. The experimental determination of this constant is described in Sec. 13.

It can be seen from formula (7.5) that $\beta = \partial \ln \Gamma_{s_0} / \partial \varepsilon_0$. Consequently, the temperature is determined by the properties of the system into which the subsystem is placed. Thus, the temperature is ■ characteristic of the system ■ a whole.

Obviously, all the parts of a system have the same temperature. Indeed, any small part of the system can be treated as a subsystem. We can then obtain for this subsystem formula (7.5) with the same value of β , i.e. all parts of the system have the same temperature. For example, if we have a mixture of gases, we can consider the components of the mixture or parts of these components as subsystems and conclude that the components of a mixture of gases have the same temperature. In other words, the mean kinetic energies of different components in a mixture of gases are equal. On the other hand, if the components are separated in space but can exchange energy, we can conclude on the basis of the above arguments that they will have the

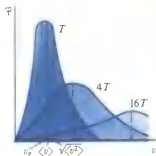


Fig. 10. Maxwell distribution

same temperature as parts of a total system. In a mixture of gases, different types of molecules have the same average kinetic energies in the thermodynamic equilibrium [see (8.14) and (8.15)]. This can be verified by direct calculations also. Let us denote the values corresponding to the first and second types of molecules by the indices 1 and 2. We take all the possible pairs of molecules and calculate their relative velocities $v_2 - v_1$, as well as the velocities of their centres of mass

$$v_{c.m.} = (m_1 v_1 + m_2 v_2) / (m_1 + m_2).$$

In view of the random nature of collisions between molecules and their rapid "loss of memory" about the preceding collisions, the velocities of the centres of mass cannot be correlated with the relative velocities. Consequently, the mean of their scalar product over all molecular pairs is equal to zero, i.e. $\langle [v_{c.m.} (v_2 - v_1)] \rangle = 0$. This gives

$$\begin{aligned} \langle [v_{c.m.} (v_2 - v_1)] \rangle &= [1/(m_1 + m_2)] [(m_1 - m_2) \langle (v_1 \cdot v_2) \rangle \\ &+ m_2 \langle v_2^2 \rangle - m_1 \langle v_1^2 \rangle] = 0. \end{aligned}$$

Since the velocities of molecules of the first and second kinds are not correlated, $\langle (v_1 \cdot v_2) \rangle$ must be equal to zero. Hence, $m_2 \langle v_2^2 \rangle = m_1 \langle v_1^2 \rangle$. In other words,

$$\langle m_1 v_1^2 / 2 \rangle = \langle m_2 v_2^2 / 2 \rangle,$$

Q.E.D.

CHARACTERISTIC VELOCITIES OF MAXWELL DISTRIBUTION. The shape of the Maxwell distribution curve is shown in Fig. 10. With increasing velocity, the peak of the distribution curve is displaced towards higher velocities, while its height becomes smaller. The presence of the peak on the curve is the result of two opposite trends: the probability of states decreases with increasing velocity, while the density of states increases. The dominating trend at low velocities is the increase in the density of states, while the tendency towards a decrease in the probability of states prevails at velocities beyond the maximum.

The average value of functions $\varphi(v)$ which depend on the absolute value of a velocity is calculated in accordance with the formula for the mean:

$$\langle \varphi \rangle = \int_0^{\infty} \varphi(v) f(v) dv. \quad (8.17)$$

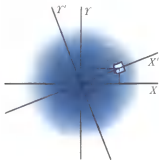


Fig. 11. To the derivation of the Gauss distribution

We can use this formula for determining $\langle v \rangle$ and $\langle v^2 \rangle$:

$$\langle v \rangle = \sqrt{8kT/(\pi m)}, \quad \sqrt{\langle v^2 \rangle} = \sqrt{3kT/m}. \quad (8.18)$$

The velocity v_p corresponding to the peak is called the most probable velocity and is determined from the condition $df(v)/dv = 0$ for the extremum. Its value is equal to

$$v_p = \sqrt{2kT/m}. \quad (8.19)$$

A comparison of (8.18) and (8.19) gives the following relation between the characteristic velocities for the Maxwell distribution:

$$\sqrt{\langle v^2 \rangle} = \sqrt{3\pi/8} \cdot \langle v \rangle = \sqrt{3/2} v_p. \quad (8.20)$$

The velocities are shown by dashed lines in the figure. Such an arrangement is due to the type of distribution, according to which a considerable contribution to $\langle v \rangle$ and $\langle v^2 \rangle$ is made by comparatively high velocities. The characteristic velocities of oxygen and nitrogen molecules in air at room temperature are 400-500 m/s. Under similar conditions, the velocities of hydrogen molecules are about 4 times higher. The molecular velocities increase with temperature as $\sqrt{T}$.

GAUSS DISTRIBUTION. The probability density of velocity in the Maxwell distribution (8.16) is determined by the quantity $\exp[-mv^2/(2kT)]$, while the factor v^2 takes into account the density of states. Distributions in which the probability densities are determined by factors of the type $\exp(-\alpha x^2)$ are encountered quite frequently in the theory of random quantities, and it is important to know the circumstances which lead to such a form of the probability distribution.

Suppose that we are shooting at a certain target with a view to hit its centre (Fig. 11). As a result of various circumstances that cannot even be enumerated, the bullets, as a rule, will not hit the centre but will be distributed symmetrically and randomly relative to the centre, since all directions are equivalent. Let us calculate their distribution. We fix the origin of the system of coordinates at the centre of the target. The causes deviating a bullet in the Y -direction do not depend on the causes deviating it in the X -direction, the two directions being equally probable. We denote the density of the probability that a bullet is deviated in the X -direction by $\varphi(x^2)$. It is clear that this quantity depends on x^2 , since the deviations in the positive and negative directions are equally probable. The probability density for deviations in the Y -direction will be $\varphi(y^2)$. Let us calculate the relative number dn/n of particles hitting an area element dS with

coordinates (x, y) . According to the probability multiplication rule, this quantity is equal to

$$dn/n = \varphi(x^2) \varphi(y^2) dS, \quad (8.21)$$

where n is the total number of particles impinging the target.

Let us now rotate the system of coordinates in such a way that the X -axis passes through the area element under consideration. In this system of coordinates, we obtain

$$dn/n = \varphi(x'^2) dS. \quad (8.22)$$

Obviously, this quantity is the same as in (8.21). Hence,

$$\varphi(x^2) \varphi(y^2) = \varphi(x'^2) = \varphi(x^2 + y^2)$$

is the functional equation for determining the form of the function φ . It must be valid for any independent variations of x and y .

Taking the logarithms of both sides and differentiating, we get

$$\frac{\varphi'(x^2)}{\varphi(x^2)} 2x dx + \frac{\varphi'(y^2)}{\varphi(y^2)} 2y dy = \frac{\varphi'(x^2 + y^2)}{\varphi(x^2 + y^2)} (2x dx + 2y dy),$$

or

$$\left[\frac{\varphi'(x^2)}{\varphi(x^2)} - \frac{\varphi'(x^2 + y^2)}{\varphi(x^2 + y^2)} \right] x dx + \left[\frac{\varphi'(y^2)}{\varphi(y^2)} - \frac{\varphi'(x^2 + y^2)}{\varphi(x^2 + y^2)} \right] y dy = 0.$$

In view of the independence of differentials, this gives

$$\frac{\varphi'(x^2)}{\varphi(x^2)} - \frac{\varphi'(x^2 + y^2)}{\varphi(x^2 + y^2)} = 0, \quad \frac{\varphi'(y^2)}{\varphi(y^2)} - \frac{\varphi'(x^2 + y^2)}{\varphi(x^2 + y^2)} = 0.$$

Consequently,

$$\frac{\varphi'(x^2)}{\varphi(x^2)} = \frac{\varphi'(y^2)}{\varphi(y^2)}.$$

Since x and y are independent, this is possible only if these expressions are equal to the same constant, i.e.

$$\frac{\varphi'(x^2)}{\varphi(x^2)} = \frac{\varphi'(y^2)}{\varphi(y^2)} = \pm \alpha. \quad (8.23)$$

?

1. How does the Maxwell distribution change with increasing temperature?
2. Why does a curve characterizing the Maxwell distribution have a maximum?
3. Why is it that all parts of a system have the same temperature at the equilibrium state?
4. What is the relation between the Maxwell and the Gauss distributions?

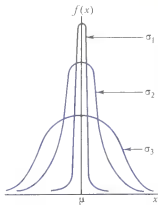


Fig. 12. The form of the Gauss distribution depending on the variance ($\sigma_1 < \sigma_2 < \sigma_3$)

Integrating these equations, we get

$$\varphi(x^2) = Ae^{\pm ax^2}, \quad \varphi(y^2) = Ae^{\pm ay^2}.$$

The function with plus sign in the exponent is not suitable as a solution, since it indicates an unlimited increase in the probability density as we go away from the centre of the target, which is obviously impossible. Denoting the square of the distance from the centre by $r^2 = x^2 + y^2$, we finally get

$$\varphi(r^2) = \varphi(x^2)\varphi(y^2) = A^2e^{-\alpha(x^2+y^2)} = A^2e^{-\alpha r^2}. \quad (8.24)$$

This distribution of probability densities is called the **Gaussian distribution**.

The exponential factor in the Maxwell distribution has a similar form (except that r^2 is replaced by v^2). The factor v^2 has nothing to do with probabilities and simply takes into account the density of states. Thus, the velocities in the Maxwell distribution deviate from the zero velocity according to the probabilistic laws exactly in the same way as the deviations of bullets from the centre of the target.

The maximum probability density in (8.24) is attained at $r = 0$. If this maximum lies at $r = \mu$ we get

$$f(x) = Be^{-\alpha(x-\mu)^2}, \quad (8.25)$$

where the random variable is denoted by x . Taking into account the value of the integral

$$\int_{-\infty}^{\infty} e^{-x^2} dx = \sqrt{\pi},$$

from the normalization condition

$$\begin{aligned} 1 &= \int_{-\infty}^{\infty} f(x) dx = B \int_{-\infty}^{\infty} e^{-\alpha(x-\mu)^2} dx = \frac{B}{\sqrt{\alpha}} \int_{-\infty}^{\infty} e^{-\xi^2} d\xi \\ &= B \sqrt{\frac{\pi}{\alpha}} \end{aligned}$$

we find $B = \sqrt{\alpha/\pi}$, whence

$$f(x) = (\alpha/\pi)^{1/2} \exp[-\alpha(x-\mu)^2].$$

Let us calculate the mean value of x and the variance σ^2 :

$$\begin{aligned} \langle x \rangle &= (\alpha/\pi)^{1/2} \int_{-\infty}^{\infty} x \exp[-\alpha(x-\mu)^2] dx \\ &= (\alpha/\pi)^{1/2} \int_{-\infty}^{\infty} (\xi + \mu) \exp(-\alpha\xi^2) d\xi = \mu; \end{aligned} \quad (8.26)$$

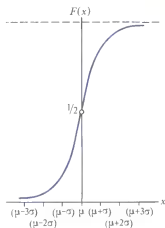


Fig. 13. Distribution of the Gauss probability function

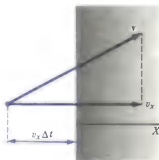


Fig. 14. To the calculation of the number of molecular collisions against the wall

$$\sigma^2 = \langle (x - \mu)^2 \rangle$$

$$= (\alpha/\pi)^{1/2} \int_{-\infty}^{\infty} (x - \mu)^2 \exp[-\alpha(x - \mu)^2] dx = 1/(2\alpha). \quad (8.27)$$

Thus, $\alpha = 1/(2\sigma^2)$, and the probability density distribution can be written in the standard form:

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{x - \mu}{\sigma}\right)^2\right]. \quad (8.28)$$

Figure 12 shows this distribution and the density for different values of σ . The smaller the standard deviation σ , the higher and narrower the maximum.

In accordance with definition (2.21), the probability distribution function has the form

$$F(x) = \frac{1}{\sigma\sqrt{2\pi}} \int_{-\infty}^x \exp\left[-\frac{1}{2}\frac{(x - \mu)^2}{\sigma^2}\right] dx. \quad (8.29)$$

This function represents the Gaussian, or normal, distribution.

Using the substitution $z = (x - \mu)/\sigma$, we can transform the above equation as follows:

$$\Phi(z) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^z e^{-z^2/2} dz. \quad (8.30)$$

This is the standard form of the normal distribution. There are tables from which the values of $\Phi(z)$ can be found. The function $F(x)$ has the form shown in Fig. 13.

THE FREQUENCY OF MOLECULAR IMPACTS AGAINST THE WALL. We direct the X -axis perpendicularly to the wall (Fig. 14) and denote the concentration of molecules by n_0 . Then the flux density of molecules moving towards the wall with velocities between v and $v + dv$ will be equal to

$$n_0 f(v) v_x^{(+)} dv, \quad (8.31)$$

where $v_x^{(+)}$ is the velocity component along the positive direction of the X -axis (molecules whose velocities are directed away from the wall do not participate in the formation of the flux). In this case, the frequency of impingements of molecules on the unit area of the vessel wall

is

$$\begin{aligned}
 v &= n_0 \int f(v) v_x^{(+)} dv \\
 &= n_0 \left(\frac{m}{2\pi kT} \right)^{3/2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-m(v_x^2 + v_y^2)/(2kT)} dv_y dv_z \\
 &\times \int_0^{\infty} e^{-mv_x^2/(2kT)} v_x dv_x = n_0 \left(\frac{kT}{2\pi m} \right)^{1/2}.
 \end{aligned} \quad (8.32)$$

With the help of formula (8.18), we finally get

$$v = n_0 \langle v \rangle / 4 \quad (8.33)$$

NUMBER OF MOLECULES IN DIFFERENT REGIONS OF THE MAXWELL DISTRIBUTION. If n_0 is the density of molecules, the number $N(v_1, v_2)$ of molecules with velocities between v_1 and v_2 will be equal to

$$N(v_1, v_2) = n_0 \int_{v_1}^{v_2} f(v) dv = n_0 \frac{4}{\sqrt{\pi}} \int_{v_1/v_p}^{v_2/v_p} e^{-u^2} u^2 du. \quad (8.34)$$

When deriving this equation, we have replaced $\exp[-mv^2/(2kT)]$ in $f(v)$ by $\exp(-v^2/v_p^2)$ in accordance with (8.19). This expression is more suitable in the analysis of the shape of the Maxwell distribution curve. There are tables for the integral

$$\varphi(x) = \frac{4}{\sqrt{\pi}} \int_x^{\infty} e^{-u^2} u^2 du. \quad (8.35)$$

With the help of this expression, we can calculate the value of (8.34) by using the following obvious relation:

$$N(v_1, v_2) = n_0 [\varphi(v_2/v_p) - \varphi(v_1/v_p)]. \quad (8.36)$$

In particular, we obtain the following values from the tables:

$$N(v_p, \infty) = 0.5724n_0; \quad N(0.5v_p, 1.5v_p) = 0.7053n_0;$$

$$N(2v_p, \infty) = 0.0460n_0.$$

Thus, a large fraction of all molecules has velocities lying in a small interval in the vicinity of the most probable velocity. The number of molecules whose velocities are considerably different from the most probable velocity is very small.

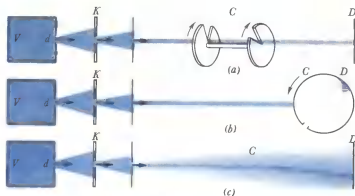
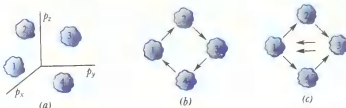


Fig. 15. Schematic diagram of experiments on the verification of the Maxwell distribution

EXPERIMENTAL VERIFICATION OF THE MAXWELL DISTRIBUTION. In view of the fundamental importance of the Maxwell distribution in statistical physics, it was subjected many times to thorough experimental verification. The block diagram of a typical experimental setup consists in the following. A gas in a steady-state equilibrium is contained in a vessel V (Fig. 15). A beam of molecules under investigation escapes through the hole d . The molecules must move without practically interacting with one another if their distribution in the beam is to remain unchanged. Hence, a high vacuum is created in the path of the beam, while the gas in the vessel V is at a low pressure. The molecules in the beam emerging from the vessel have the same velocity distribution as in the vessel if we can ensure a gas flow through the hole d without any hydrodynamic pressure. This is possible if the molecules do not have time to collide with each other in the region surrounding the hole. In this case a molecule incident on the hole escapes from the vessel without perturbing the states of the remaining molecules in the vessel. Consequently, the number of molecules in the vessel decreases slowly, although their equilibrium state remains unchanged. In order to ensure such a "collision-free" departure of molecules from the vessel, the size of the hole d should be much smaller than the mean free path of the molecules (the mean distance between successive collisions, see Sec. 50).

An idea of the order of magnitude of the quantities can be got if we consider that under normal conditions molecules in air undergo about 10^9 collisions per second, while their mean free path is of the order of 10^{-7} m. The mean free path increases with decreasing pressure, and hence the diameter d of the hole must be very small. In experiments involving

Fig. 16. Schematic diagram of particle exchange, incompatible with the detailed balancing principle



molecular beams, its value is a few hundredths of a millimeter. The density of the molecular flux along the beam is given by the expression (8.31).

After leaving the hole d , the beam passes through the collimator C which consists of consecutive slits and isolates the molecules moving almost in parallel. This is followed by the device S for sorting molecules according to their velocities, and the detector D for registering molecules after they have been sorted.

The molecules are usually sorted by using the method of rotating discs with slits along the radius (Fig. 15a). This method was employed in the 19th century by Fizeau for determining the velocity of light in terrestrial conditions. If the slits are rotated at an angle α with respect to each other, and if l is the distance between the discs, the discs will be rotated by the angle ϖ in a time $\Delta t = \alpha/\omega$, where ω is the angular velocity of the disc. Hence, molecules passing through both the slits will have velocities $v = l/\Delta t = l\omega/\alpha$ and $v_n = l\omega/(\alpha + 2\pi n)$ (where $n = 1, 2, \dots$) corresponding to several revolutions of the discs while the molecules traverse the distance l . The molecules are registered by different methods, depending on their properties. In the simplest case they are deposited on a screen, and the thickness of the deposited layer is used for determining the number of molecules. This method is employed, for example, when the object of investigation is a beam of silver atoms obtained in the volume V as a result of evaporation upon heating.

In another method (Fig. 15b), the selector and the detector are combined in a rotating cylinder with a slit. When the slit coincides with the direction of the beam, a part of molecules enters the cylinder through it. Molecules with different velocities arrive at the opposite wall of the cylinder at different instants with respect to the moment of passage through the slit, and hence arrive at different parts of the inner wall of the cylinder. A measurement of the number of molecules falling on different regions can yield the velocity distribution of molecules in the beam.

?

5. What is the essence of the detailed balancing principle?
6. The Maxwell distribution allows infinitely large velocities and kinetic energies of molecules. In what way is this compatible with the finite total kinetic energy of the gas molecules?
7. Due to which properties of the Maxwell distribution is the mean absolute velocity higher than the most probable velocity but lower than the root-mean-square velocity?



Fig. 17. Schematic diagram of particle exchange, corresponding to the detailed balancing principle

In one of the most elegant experiments, the force of gravity was used as a selector (Fig. 15c). Slow molecules deviate towards the Earth to a larger extent than faster molecules in a gravitational field. The deviation can be easily calculated as a function of velocity. In an actual experiment of this kind, these deviations were of the order of several tenths of a millimeter. However, it was possible to carry out such measurements reliably.

The experimental results confirm the validity of the Maxwell distribution.

DETAILED BALANCING PRINCIPLE. The Maxwell distribution is an equilibrium, and hence stationary, state which does not vary with time. This means that the number of particles in each volume element dv_x , dv_y , dv_z in the vicinity of the velocity v in the velocity space does not change with time. However, molecules undergo collisions as a result of which the number of molecules in each volume element continuously changes, although their average number remains constant. Hence, the number of particles arriving per unit time at each volume element in the velocity space is equal to the number of particles leaving it. It can be asked as to which volume elements form the origin or destination of these particles. One can theoretically consider several ways in which the number of particles in all volume elements remains constant.

Let us consider, for example, any four volume elements 1-4 (Fig. 16a) and imagine that these elements mutually exchange particles. Each arrow represents a certain number of particles leaving a certain volume or arriving in it per unit time. For example, in Fig. 16b particles from the volume element 1 depart for the volume element 2, but an equal number of particles arrive at this element from element 4, and so on. In Fig. 16c, particles from elements 2 and 4 arrive at element 3, but an equal number of particles goes over from this element to element 1. As a result of the exchange of particles shown in the figure, it can be ensured that the number of particles in all the volume elements remains constant.

However, the state of equilibrium cannot be attained as a result of such exchanges. According to the detailed balancing principle, the equilibrium is attained in a detailed manner, i.e. over all the pairs of volume elements. This means that each volume element gives away to any other volume element as many particles per unit time as it receives in return. Hence, the only possible diagram according to which four volume elements can mutually exchange particles is the one shown in Fig. 17. Generally speaking, the intensity

of exchange between each pair of volume elements is different.

The validity of the detailed balancing principle is due to the fact that the equilibrium state is attained as a result of the chaotic nature of collisions and disorderliness in the motion of molecules. The diagrams shown in Fig. 16 are unrealizable, since the exchanges shown in these diagrams can take place only as a result of certain ordering in the motion of molecules and in their mutual collisions. The detailed balancing principle is valid not only for collisions but also for all other processes in all systems in which the equilibrium state can be attained as a result of completely chaotic processes.

Example 8.1. Find the number of oxygen molecules whose velocities lie between 195 and 205 m/s at 0 °C. The mass of oxygen is 0.1 kg.

Since the interval of velocities (from 195 to 205 m/s) is quite small, we can use the mean value theorem and write, in accordance with (8.16),

$$\frac{\Delta n}{n} \sim 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-mv^2/(2kT)} v^2 dv, \quad (8.37)$$

where $v = 200$ m/s and $dv = 10$ m/s.

The relative molecular mass $M_r = 32$. Consequently, the mass of an oxygen molecule $m = 32 \times 1.66 \times 10^{-27}$ kg = 5.31×10^{-26} kg. The molar mass of oxygen $M = 32 \times 10^{-3}$ kg/mole. Hence, 0.1 kg of oxygen contains $n = [0.1/(32 \times 10^{-3})] \times 6.02 \times 10^{23} = 1.88 \times 10^{24}$ molecules. Further, we consider that $kT = 1.38 \times 10^{-23} \times 273$ J = 3.77×10^{-21} J. Hence,

$$\begin{aligned} \Delta n &= 4 \times 3.14 \left(\frac{5.31 \times 10^{-26}}{6.28 \times 3.77 \times 10^{-21}} \right)^{3/2} \\ &\times \exp \left[- \frac{5.31 \times 10^{-26} (200)^2}{2 \times 3.77 \times 10^{-21}} \right] \times (200)^2 \times 10 \times 1.88 \times 10^{24} \\ &= (2.2 \times 10^{-6})^{3/2} \exp(-0.28) \times 9.44 \times 10^{30} \\ &= 3.08 \exp(-0.28) \times 10^{22} = 2.3 \times 10^{22}. \end{aligned}$$

Sec. 9. BOLTZMANN DISTRIBUTION

The peculiarities of the Boltzmann distribution are discussed together with some of its simplest applications. The relation between the Boltzmann distribution and the Maxwell distribution are analyzed. Experimental verification of the Boltzmann distribution is described.

INDEPENDENCE OF THE PROBABILITY DENSITIES OF THE COORDINATES AND VELOCITIES OF PARTICLES. If a gas is in an external potential field, the particle energy ε_x appearing in formula (7.6) is equal to

$$\varepsilon_x = mv^2/2 + U. \quad (9.1)$$

The number of states in an element of the phase space is given by formula (8.1). Hence, instead of formula (8.2), we obtain

$$\begin{aligned} d\mathcal{P}(x, y, z, p_x, p_y, p_z) &= \frac{A}{(2\pi h)^3} \\ &\times \exp\left[-\beta\left(\frac{mv^2}{2} + U\right)\right] dx dy dz dp_x dp_y dp_z. \end{aligned} \quad (9.2)$$

Obviously, the probability densities of the coordinates and momenta of a particle are independent. Consequently,

$$d\mathcal{P}(x, y, z, p_x, p_y, p_z) = d\mathcal{P}_1(x, y, z) d\mathcal{P}_2(p_x, p_y, p_z), \quad (9.3)$$

where

$$d\mathcal{P}_1(x, y, z) = A_1 \exp[-\beta U(x, y, z)] dx dy dz,$$

$$d\mathcal{P}_2(p_x, p_y, p_z) = A_2 \exp(-\beta mv^2/2) dp_x dp_y dp_z.$$

As usual, the constants A_1 and A_2 are obtained from the normalization condition. The formula for $d\mathcal{P}_2(p_x, p_y, p_z)$ was discussed in Sec. 8 and leads to the Maxwell distribution, while the formula for $d\mathcal{P}_1(x, y, z)$ leads to the Boltzmann distribution.

BOLTZMANN DISTRIBUTION. The quantity $d\mathcal{P}_1(x, y, z)$ in (9.3) defines the probability that a particle is located in the volume element $dx dy dz$ in the vicinity of the point (x, y, z) . Just as in the derivation of the Maxwell distribution in Sec. 8, we go over to a system of n particles, i.e. we consider that the particles are independent and use the probability distribution formulas.

If the total number of particles in a canonical system is n , we obtain from the probability multiplication rule for a volume element $dx dy dz$ in the vicinity of the point (x, y, z)

$$dn(x, y, z) = A_1 n \exp[-U(x, y, z)/(kT)] dx dy dz. \quad (9.4)$$



Ludwig Eduard
Boltzmann
(1844-1906)

The constant A_1 is found from the normalization condition which in the present case means that there are n particles in the volume $dx dy dz$:

$$\int_V dn = A_1 n \int_V \exp[-U(x, y, z)/(kT)] dx dy dz = n. \quad (9.5)$$

Consequently,

$$\frac{1}{A_1} = \int_V \exp[-U(x, y, z)/(kT)] dx dy dz. \quad (9.6)$$

The formula

$$\frac{dn}{n dx dy dz} = A_1 \exp[-U(x, y, z)/(kT)] \quad (9.7)$$

is called the **Boltzmann distribution**. It describes the distribution of the concentration of particles in space as a function of their potential energy.

It is not always necessary to calculate the normalization constant A_1 since we are often interested only in the distribution of the concentration of particles and not in their total number. Suppose that the concentration of particles at the point (x_0, y_0, z_0) is given by $n_0 = n_0(x_0, y_0, z_0) = dn/(dx_0 dy_0 dz_0)$. The potential energy at this point is $U_0 = U(x_0, y_0, z_0)$. We denote the particle concentration at the point (x, y, z) by $n_0(x, y, z)$. Then formula (9.7) for these two points has the form

$$\frac{n_0(x_0, y_0, z_0)}{n} = A_1 \exp[-U_0/(kT)], \quad (9.8a)$$

$$\frac{n_0(x, y, z)}{n} = A_1 \exp[-U(x, y, z)/(kT)]. \quad (9.8b)$$

Substituting the value of A_1 obtained from (9.8a) into (9.8b), we obtain

$$n_0(x, y, z) = n_0(x_0, y_0, z_0) \exp\{-[U(x, y, z) - U_0]/(kT)\}.$$

(9.9)

This is the most commonly used form for the Boltzmann formula. It is especially convenient to choose the normalization for the potential energy in such a way that at the point (x_0, y_0, z_0) the potential energy is equal to zero ($U_0 = 0$).

Formula (9.9) is essentially equivalent to (9.7). If the concentration of gas molecules is not known at any point, and only the total number of molecules in the given volume is known, $n_0(x_0, y_0, z_0)$ is constant and is determined from the normalization condition for the total number of particles in the volume.

MIXTURE OF GASES IN A VESSEL. Suppose that two types of molecules are contained in a closed cylindrical vessel with the base area S and height h_0 . The total number of molecules of the first and second types is denoted by n_1 and n_2 , and their corresponding masses are m_1 and m_2 . Let us find the distribution of molecules over the height of the cylinder.

In the first place, it is obvious that the probability density of the location of a molecule of a certain type is independent of the position of not only the other molecules of the same type, but of molecules of the other type as well. Hence the distribution of each type of molecules is given by formula (9.9). We denote the height of a molecular layer from the bottom of the vessel by h . The concentration of molecules depends only on h . It is convenient to normalize the potential energy of the molecules to zero at the bottom of the vessel ($h = 0$). Under such a normalization, the potential energy of the molecules at the height h is equal to $U = mgh$. Consequently, the distribution (9.9) of the concentration of molecules with the height has the form

$$\begin{aligned} n_{01}(h) &= n_{01}(0) \exp[-m_1 gh / (kT)], \\ n_{02}(h) &= n_{02}(0) \exp[-m_2 gh / (kT)]. \end{aligned} \quad (9.10)$$

From the normalization condition

$$S \int_0^{h_0} n_{01}(h) dh = n_1, \quad S \int_0^{h_0} n_{02}(h) dh = n_2 \quad (9.11)$$

we obtain

$$\begin{aligned} n_{01}(0) &= \frac{n_1 m_1 g}{SkT} \left[1 - \exp\left(-\frac{m_1 gh_0}{kT}\right) \right]^{-1}, \\ n_{02}(0) &= \frac{n_2 m_2 g}{SkT} \left[1 - \exp\left(-\frac{m_2 gh_0}{kT}\right) \right]^{-1}. \end{aligned} \quad (9.12)$$

The ratio the concentrations of molecules at different heights is equal to

!

The energy of molecules moving upwards in a gravitational field decreases, but in the case of the Maxwell velocity distribution the mean energy per molecule does not change. The constant value of the mean energy per molecule can be maintained in spite of a decrease in the energy of individual molecules due to the escape of "less energetic" particles from the particle flux in ascending motion. The mean energy of molecules moving downwards does not change since the particles escaping from the flux in the upward motion join the downward flux.

$$\frac{n_{02}(h)}{n_{01}(h)} = \frac{n_2 m_2}{n_1 m_1} \frac{1 - \exp[-m_1 g h_0 / (kT)]}{1 - \exp[-m_2 g h_0 / (kT)]} \exp\left[-\frac{(m_2 - m_1)gh}{kT}\right]. \quad (9.13)$$

It can be seen from formula (9.10) that the concentration of heavier molecules decreases with height more rapidly than for the lighter molecules. Formula (9.13) shows that the heavier gas is concentrated near the bottom of the vessel, while the lighter gas is concentrated near the top.

Let us estimate the order of magnitude of the quantities. It is well known that under normal conditions, the concentration of molecules in air is equal to $n_0 = 2.7 \times 10^{25} \text{ m}^{-3}$. For the sake of definiteness, we shall assume the second gas to be oxygen, while hydrogen is assumed to be the first. The temperature T of the air is equal to 300 K ($t = 27^\circ\text{C}$), $m_1 = 3.34 \times 10^{-27} \text{ kg}$, $m_2 \simeq 16 m_1$, $kT \simeq 4.14 \times 10^{-21} \text{ J}$, and $g \simeq 9.8 \text{ m/s}^2$. Under these conditions, the exponents for not very large values of h are extremely small.

For example, $m_1 g h / (kT) \simeq 8 \times 10^{-6} h$, and $m_2 g h / (kT) \simeq 10^{-4} h$. We can expand the exponential terms into a series and retain only the linear term in h :

$$\frac{n_{02}(h)}{n_{01}(h)} \sim \left[1 - \frac{(m_2 - m_1)}{kT} g h\right] \sim (1 - 1.2 \times 10^{-4} h). \quad (9.14)$$

Thus, the molecular concentration of the heavier component decreases in the upper part of the vessel, while that of the lighter component increases. This is clearly noticeable for large values of h . Suppose that $h \simeq 10^4 \text{ m}$. In this case, formula (9.13) assumes the form

$$\frac{n_{02}(h)}{n_{01}(h)} \sim \exp(-1.2 \times 10^{-4} h). \quad (9.15)$$

Since $\exp(-1.2) \simeq 0.3$, the ratio of the concentrations of particles changes by more than three times from 0 to 10^4 m . It should be also noted that although the change in concentration with height is very small for a small difference in heights, it nevertheless is responsible for the emergence of the lifting force for flying machines that are lighter than air (see Sec. 10).

RELATION BETWEEN THE BOLTZMANN AND MAXWELL DISTRIBUTIONS. The Maxwell and Boltzmann distributions are parts of the Gibbs distribution. The temperature is determined by the mean kinetic energy. Hence it can be asked as to why the temperature is constant in a potential field although according to the law of conservation of energy the kinetic energy of particles must change if their potential energy changes, and consequently, as it appears at a first glance, the temperature of the particles also must change. In other words, we can ask the following questions: during the upward motion of particles in a gravitational field, why does their kinetic energy decrease while their temperature (i.e. their mean kinetic energy) remains constant? Why does the energy of all the particles increase during their downward motion while their mean energy remains constant?

This can be explained as follows. In the case of upward motion, the slowest (i.e. the "coldest") particles escape from the total flux of particles. Hence the mean energy is calculated over a smaller number of particles which on the average were "hotter" at the initial height. In other words, if a certain number of particles arrive at the height h from the bottom, the mean energy of these particles at the height h will be equal to the mean energy of all the particles at the bottom, a part of which could not escape to the height h due to inadequate kinetic energy. However, if we calculate at the zero height the mean energy of particles that have reached the height h , it turns out to be higher than the average energy of all particles at the zero height. Hence we can say that the mean energy of particles at the height h indeed became lower, and in this sense they were "cooled" during the ascent. However, the mean energy of all particles at the zero height and at the height h is the same, i.e. the temperature is also the same. On the other hand, a decrease in number density of the particles with height is also a result of escape of particles from the flux.

Consequently, the law of conservation of energy as applied to the upward motion of particles leads to a decrease in their kinetic energies and to the escape of particles from the flux. As a result, the density of particles decreases with height on the one hand, while on the other hand their kinetic energy is conserved in spite of the fact that the kinetic energy of each particle decreases. This can be verified by a direct calculation which we recommend to the reader as an exercise.

ATMOSPHERE OF PLANETS. The potential energy of a particle of mass m in the gravitational field of a spherical

?

1. The kinetic energy of particles moving upwards in the gravitational field decreases. Why is the temperature in the gravitational field in equilibrium independent of height?
2. How can be Boltzmann distribution be applied to a gas mixture?
3. How are the Boltzmann and Maxwell distributions interrelated?

celestial body is equal to

$$U(r) = -G \frac{Mm}{r}, \quad (9.16)$$

where M is the mass of the body, r is the distance from the centre of the body to the particle, and G is the gravitational constant. The atmosphere of planets (including the Earth) is not in an equilibrium state. For example, one of the consequences of a nonequilibrium state of the Earth atmosphere is the fact that its temperature is not constant as it should be but varies with height (decreases with increasing height). We shall show that the atmosphere of a planet cannot in principle be in an equilibrium state. If the opposite were true, the density of the atmosphere should change with height in accordance with formula (9.9) which in this case assumes the form

$$n_0(r) = n_0(r_0) \exp \left[-G \frac{mM}{kT} \left(\frac{1}{r_0} - \frac{1}{r} \right) \right], \quad (9.17)$$

where we took into account expression (9.16) for the potential energy, and r_0 is the radius of the planet. According to this formula, the density tends to a finite limit as $r \rightarrow \infty$:

$$n_0(r \rightarrow \infty) \rightarrow n_0(r_0) \exp \left(-G \frac{mM}{kT} \frac{1}{r_0} \right). \quad (9.18)$$

This means that if there is a finite number of molecules in the atmosphere, they should be distributed over the entire infinite space, i.e. the atmosphere is diffused.

Since any system ultimately tends to an equilibrium state, the atmospheres of planets gradually dissipate. Some celestial bodies such as the Moon completely lost their atmospheres, while the others, like the Mars, have a very rarefied atmosphere. Thus, the Moon's atmosphere has already attained the equilibrium state, and the Mars' atmosphere is close to it. The atmosphere of the Venus is very dense and hence is at the beginning of its way towards the equilibrium state.

In order to consider quantitatively the loss of atmosphere in planets, we must take into account the velocity distribution of molecules. Only those molecules can overcome the gravitational force whose velocities exceed the escape velocity. These molecules are in the "tail" of the Maxwell

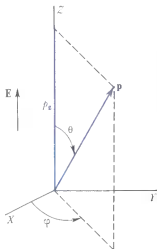


Fig. 18. To the calculation of the polarization of polar dielectrics

distribution, and their relative number is not large. Nevertheless, over considerable intervals of time the loss of molecules becomes noticeable. Since the escape velocity for heavy planets is higher than for light ones, heavy celestial bodies lose their atmosphere to a smaller extent than light planets, i.e. light planets lose their atmospheres quicker than heavier ones. The time during which a planet loses the atmosphere depends on its radius, temperature, composition of its atmosphere, and other factors. A complete quantitative analysis of this phenomenon is a very complicated problem.

TEMPERATURE DEPENDENCE OF POLARIZATION OF POLAR DIELECTRICS. Polar dielectrics are the materials whose molecules have a permanent dipole electric moment. A dipole is a system of two equal and opposite charges separated by a distance l (Fig. 18). The dipole moment $p = |q|l$ is a vector directed from the negative to positive dipole charge, and $|q|$ is the absolute magnitude of the dipole charges. Normally, the dipole moment is of the order of $\sim 10^{-30}$ C·m. For example, the dipole moment of an HCl molecule is about 3.44×10^{-30} C·m, for HBr it is 2.33×10^{-30} C·m, and so on. In an external electric field, dipoles tend to orient in the direction of the field. As a result, the dielectric is polarized, i.e. acquires a macroscopic dipole moment characterized by the polarization vector. The polarization vector is equal to the sum of molecular dipole moments in a small volume, divided by this volume.

In contrast to the external electric field, thermal motion of molecules tends to disturb the orientation of the dipoles. As a result, the dipole moments are randomly oriented with respect to the direction of the electric field. We shall try to find the angular distribution of dipole moments with respect to the electric field and the dependence of the polarization vector on the temperature.

It is known from the theory of electricity that a dipole (with dipole moment p) placed into an electric field of intensity E has the potential energy

$$U = -p \cdot E. \quad (9.19)$$

The simplest way to derive this formula is as follows. We direct the Z-axis along the electric field. The forces acting on the charges forming the dipole are directed along the Z-axis (Fig. 18) and equal to qE and $-qE$ (here q is assumed to be the magnitude of the charge). The general relation between forces and the potential energy yields the expressions for the potential energies of the two charges: $U(z_2) = -qEz_2$ and

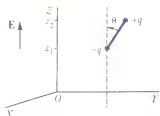


Fig. 19. To the calculation of the dipole energy in an electric field

$U(z_1) = qEz_1$. Hence, the energy of the dipole (in the uniform field) is

$$U = U(z_2) + U(z_1) = -qE(z_2 - z_1) = -qEl \cos \theta = -p \cdot E.$$

This formula is also valid for the energy of a dipole in an alternating electric field, since it does not depend on the derivatives with respect to coordinates, and the separation between dipole charges can be infinitely small.

Obviously, the angular distribution of dipoles is symmetric with respect to the Z-axis and depends on the angle θ (Fig. 19). The potential energy depends on θ and does not depend on the coordinates (the field intensity E is considered to be constant within a volume element for which the angular distribution is calculated). Denoting the solid angle element by $d\Omega$, we can rewrite formula (9.4) for the Boltzmann distribution in the form

$$dn(d\Omega) = Ae^{p \cdot E / (kT)} d\Omega = Ae^{pE \cos \theta / (kT)} d\varphi \sin \theta d\theta, \quad (9.20)$$

where A is the normalization constant, and the expression $d\Omega = d\varphi \sin \theta d\theta$ for the solid angle in the spherical coordinates is used. This formula gives the solution to the problem on the angular distribution of dipole moments.

Due to the axial symmetry, the mean dipole moment has a component only along the Z-axis:

$$\begin{aligned} \langle p_z \rangle &= \frac{\int_0^\pi p \cos \theta \exp(\alpha \cos \theta) \sin \theta d\theta}{\int_0^\pi \exp(\alpha \cos \theta) \sin \theta d\theta} \\ &= \frac{\partial}{\partial \alpha} \int_0^\pi p \exp(\alpha \cos \theta) \sin \theta d\theta, \end{aligned} \quad (9.21)$$

where $\alpha = pE/(kT)$. Then

$$\langle p_z \rangle = pL(\alpha), \quad L(\alpha) = \coth \alpha - 1/\alpha. \quad (9.22)$$

The form of the function $L(\alpha)$, called the Langevin function, is shown in Fig. 20. The series expansion of hyperbolic cotangent has the form

$$\coth \alpha = 1/\alpha + \alpha/3 - \alpha^3/45 + \dots \quad (9.23)$$

In the case of comparatively weak fields for which $pE \ll kT$, we can confine ourselves to the linear term, which considerably simplifies formula (9.22):

$$\langle p_z \rangle = p^2 E / (3kT). \quad (9.24)$$

$$\begin{aligned} n_0(x, y, z) \\ = n_0(x_0, y_0, z_0) \\ \times e^{[-U(x, y, z) - U_0]/(kT)} \end{aligned}$$

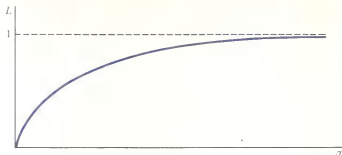


Fig. 20. The Langevin function

The polarization vector is directed along the Z-axis, and its magnitude is equal to the product of expression (9.24) and the atomic density. Thus, the polarization of polar dielectrics is inversely proportional to the temperature.

We have considered this example in order to illustrate the applicability of the Boltzmann distribution not only for the analysis of the spatial distribution of particles but also for the analysis of their distribution over other parameters which can determine their potential energy.

EXPERIMENTAL VERIFICATION OF THE BOLTZMANN DISTRIBUTION. When deriving the Boltzmann distribution, we imposed no restriction on the mass of the particles. Hence, it can in principle be applied to heavy particles as well. Let us consider grains of sand as such particles. Clearly, they will form a certain layer near the bottom of the vessel. Strictly speaking, this is a consequence of the Boltzmann distribution. For large masses, the exponent changes with height so rapidly that it becomes equal to zero everywhere beyond the layer of sand. As regards the region within the layer, we must take into account the volume of the grains of sand. The problem will then be reduced to a purely mechanical problem of determining the minimum of the potential energy with given constraints. Such problems are considered in mechanics rather than in statistical physics.

In order to prevent heavy particles from "falling to the bottom" and obtain their distribution over height in a sufficiently thick layer, we must somehow decrease their potential energy. This can be done by placing the particles into a liquid whose density is only slightly lower than the density of the material of the particles. By denoting the density and the volume of the particles by ρ and τ and the density of the liquid by ρ_0 , we find that the force acting on a particle is equal to $\tau(\rho - \rho_0)g$. Consequently, the potential energy of such a particle at a height h from the bottom of the

vessel is

$$U(h) = \tau(\rho - \rho_0)gh. \quad (9.25)$$

Hence the distribution of concentration of these particles over height is given by

$$n_0(h) = n_0(0) \exp[-\tau(\rho - \rho_0)gh/(kT)]. \quad (9.26)$$

To make the effect noticeable, the particles must be sufficiently small. The number of such particles at various heights in the vessel is counted with the help of a microscope. The first experiments of this type were carried out in 1906 by J. Perrin (1870-1942).

After taking measurements, we can verify whether the concentration of particles varies with height according to the exponential law. Perrin proved that this is really so, and hence the Boltzmann distribution is valid. Further, proceeding from this assumption and measuring by independent methods the volumes and densities of particles, we can use the results of the experiment to find the value of the Boltzmann constant k since other quantities in (9.26) are known. The value of k obtained by Perrin is very close to its present-day value. Perrin also measured k by another independent method based on the Brownian movement.

Later, other types of experiments completely confirmed the Boltzmann distribution. Among these experiments we can mention, for example, the verification of the temperature dependence of the polarization of polar dielectrics considered above.

Example 9.1. For determining the Avogadro constant, Perrin used the distribution of gamboge gum grains in water. The density of the gamboge gum particles was $\rho = 1.21 \times 10^3 \text{ kg/m}^3$, and their volume $\tau = 1.03 \times 10^{-19} \text{ m}^3$. The temperature during the experiment was 4°C . Find the height h at which the density of grain distribution decreased to $\frac{1}{2}$ half of the initial value.

Considering that $\tau(\rho - \rho_0) = 0.22 \times 10^{-16} \text{ kg}$, we obtain from formula (9.26)

$$h = kT \ln 2 / [\tau(\rho - \rho_0)g] = 12.3 \cdot 10^{-6} \text{ m}.$$

Example 9.2. Spherical particles of radius 10^{-7} m are suspended in air at temperature 0°C and pressure $1.013 \times 10^5 \text{ Pa}$. The particle concentration was found to decrease to half at the height of 20 m. Find the mass of a suspended particle.

By using formula (9.26), we find $\tau(\rho - \rho_0) = kT \ln 2/(gh) = 1.33 \times 10^{-23}$ kg.

Considering that $\tau = 4.19 \times 10^{-21}$ m³, we find $\rho - \rho_0 = 3.2 \times 10^{-3}$ kg/m³. Since $\rho_0 = 1.293$ kg/m³, we get $\rho = 1.296$ kg/m³, and hence the mass of a particle is $m = 1.296 \times 4.19 \times 10^{-21}$ kg = 5.43×10^{-21} kg.

Sec. 10. PRESSURE

The basic equation of the kinetic theory of gases is derived and its different forms and regularities connected with them are discussed.

The barometric formula is analyzed and the mechanisms of lifting force acting on balloons and aerostats are considered. The principal methods of measuring pressure in various ranges are described.

THE BASIC EQUATION OF THE KINETIC THEORY OF GASES. Pressure is created as a result of impacts of molecules against the vessel walls. Each molecule imparts to the wall the momentum by which the momentum of this molecule changes as a result of the collision with the wall. Hence, if we direct the X -axis along the normal to the wall (see Fig. 14), the momentum transmitted in one collision is $2mv_x^{(+)}$ (m is the mass of the molecule). Pressure is equal to the momentum imparted to the wall of area 1 m² by the molecules striking the wall per second. Therefore, the pressure is equal to twice the momentum flux of molecules, normal to the surface of the wall.

According to (8.31), the momentum flux towards the wall, created by the molecules whose absolute velocities lie between v and $v + dv$ is

$$n_0 f(v) v_x^{(+)} dv m v_x^{(+)}. \quad (10.1)$$

The superscript (+) on the velocity indicates that the flux is created only by the molecules moving towards the wall (i.e. by the half of the total number of molecules). This gives

$$p_x = 2n_0 m \int f(v) (v_x^{(+)})^2 dv = n_0 kT. \quad (10.2)$$

In this formula, the integral is evaluated in exactly the same way as in (8.32) for which detailed calculations were made.

The components p_y and p_z are calculated similarly, the result being the same as (10.2):

$$p_x = p_y = p_z = p = n_0 kT. \quad (10.3)$$

As expected, the gas pressure is isotropic and can be denoted by p without specifying the direction in which it acts. Note that it is not always the case. If the mechanical properties of a medium are anisotropic, the pressure at a given point may be different in different directions. Naturally, in the case under consideration we have a gas with isotropic properties.

Let us express the temperature in (10.3) in terms of mean square velocity $\langle v^2 \rangle$ defined by formula (8.18). Then Eq. (10.3) can be written in the form

$$p = \frac{2}{3} \left\langle \frac{mv^2}{2} \right\rangle. \quad (10.4)$$

This equation is called the **basic equation of the kinetic theory of gases**.

When deriving Eq. (10.4), we made no assumption about the nature of molecular impacts against the wall. This process is very complicated and depends on the properties of molecules as well as on the properties of the wall material and its finishing. Generally speaking, the reflection of atoms at the wall does not obey the laws of the mirror reflection, i.e. the angle of incidence on the wall is not equal to the angle of reflection. In most cases the "cosine law" is observed, according to which the intensity of reflection in a certain direction is proportional to the cosine of the angle formed by this direction with the normal to the surface. This intensity is almost independent of the angle of incidence. If the surface is a face of a single crystal, the law of the reflection considerably depends on the properties of the crystal and may have minima and maxima in different directions, and so on. However, while calculating pressure it is not necessary to take into consideration all these aspects, since in the steady state tangential components of the momentum must ultimately cancel out upon averaging, while according to the momentum conservation law for a closed system, the normal components will ensure the pressure (10.4).

CLAPEYRON-MENDELEEV EQUATION. Denoting by n the total number of molecules in the volume V of a gas and considering that $n_0 = n/V$, Eq. (10.3) can be represented in the form

$$pV = nkT. \quad (10.5)$$

Since n cannot be directly measured for a given mass of the gas, we must impart to the equation a more convenient form. For this we shall use the concept of ν mole.

The total number of molecules in ν moles is equal to $n = \nu N_A$. Hence Eq. (10.5) can be written in the form

$$pV = \nu RT, \quad (10.6a)$$

where

$$R = kN_A = 8.31441 \text{ J/(mole} \cdot \text{K)} \quad (10.7)$$



Dmitrii Ivanovich
Mendeleev
(1834-1907)

! For molecules impinging a solid, the surface is different from the mirror surface and has an intricate topography determined by the properties of the solid and finishing of the surface. Therefore, the impact of a molecule or an atom on a surface is a complex process. The details of this process are not important for the analysis since the momentum conservation law for a closed system, used in this case, is always valid.

is the molar gas constant. The quantities corresponding to a mole of a substance are called molar. Equation (10.6a) is called the Clapeyron-Mendeleev equation. For $T = \text{const}$, we obtain from it Boyle's law, while for $p = \text{const}$, we get Gay-Lussac's (Charles') law.

Equation (10.6a) can be given another form if we introduce the concept of the molar volume, which is defined as the volume of a substance contained in one mole:

$$V_m = \frac{\text{volume occupied by the gas}}{\text{number of moles in the gas}} = V/\nu.$$

We can then write

$$pV_m = RT. \quad (10.6b)$$

Sometimes it is expedient to represent Eq. (10.6a) in such a form that it contains the mass explicitly. For this purpose we use equation (1.8): $M = m/\nu$, where M is the molar mass and m the mass of the substance. This gives

$$pV = \frac{m}{M} RT. \quad (10.8)$$

Equation (10.6a) was named after Clapeyron and Mendeleev because of the following circumstances. First Clapeyron presented the generalized Boyle's law in the form $pV = A(267 + t)$, where A is a constant characterizing the given mass of a gas, t is the temperature in the Celsius scale. The number 267 was introduced into this equation because Clapeyron assumed the thermal expansion coefficient to be $1/267$ and not $1/273$. Subsequently, Mendeleev improved this equation by introducing the molar gas constant and representing it in the form (10.8).

DALTON'S LAW. As was repeatedly mentioned above, individual components of a mixture can be assumed to be independent. Therefore each component creates a pressure corresponding to (10.3), the total pressure being equal to the sum of the pressures of the components:

$$p = n_{o1}kT + n_{o2}kT + \dots + n_{oi}kT = p_1 + p_2 + \dots + p_i, \quad (10.9)$$

where p_i is the partial pressure. Equation (10.9) expresses Dalton's law of partial pressures. Naturally, at sufficiently

high concentrations (pressures) of the gases we should expect that there will be deviations from Dalton's law since the interaction which actually exists between the mixture components will come into play and these components will no longer be independent. Indeed, such deviations from Dalton's law at a sufficiently high pressure are actually observed. This law was established in 1801 by Dalton (1766-1844) who explained it with the help of the atomistic hypothesis.

Denoting the partial pressures, masses and molar masses of the components of a gas mixture by p_i , m_i , and M_i respectively, Eq. (10.8) can be represented in accordance with Dalton's law (10.9) as follows:

$$(p_1 + p_2 + \dots + p_i) V = \left(\frac{m_1}{M_1} + \frac{m_2}{M_2} + \dots + \frac{m_i}{M_i} \right) RT. \quad (10.10a)$$

If we denote the pressure of the gas mixture by $p = p_1 + p_2 + \dots + p_i$, its mass by $m = m_1 + m_2 + \dots + m_i$, and introduce the mean molar mass $\langle M \rangle$ of the gas mixture from the expression $1/\langle M \rangle = (1/m)[(m_1/M_1) + (m_2/M_2) + \dots + (m_i/M_i)]$, Eq. (10.10a) can be rewritten in a form similar to Eq. (10.8) for a one-component gas:

$$pV = \frac{m}{\langle M \rangle} RT. \quad (10.10b)$$

AVOGADRO'S LAW. The equation of state for an ideal gas written in the form (10.5) shows that equal volumes of all gases measured at the same temperature and pressure contain the same number of molecules. This statement, which was formulated in 1811, is called *Avogadro's law*.

Consequently, a mole of any gas at a given temperature and pressure occupies the same volume. Under standard conditions ($p = 101.325 \text{ kPa}$ and $T = 273.15 \text{ K}$) this volume is equal to

$$V_m = (RT/p) = 22.41383 \cdot 10^{-3} \text{ m}^3/\text{mole}.$$

The concentration of molecules under these conditions is given by *Loschmidt number*

$$N_L = 2.686754 \cdot 10^{25} \text{ m}^{-3}.$$

BAROMETRIC FORMULA. Since formula (10.3) unambiguously gives pressure in terms of temperature, we can use the Boltzmann distribution to immediately find the distribution of pressure under the same conditions for which this formula is valid, i.e. in equilibrium conditions ($T = \text{const}$). Hence, for isothermal atmosphere the variation of pressure of each component with height h is described by the formulas

$$p_i(h) = n_{oi}(h) kT, \quad p_i(h) = p_i(0) \exp[-m_i gh/(kT)]. \quad (10.11)$$

Atmospheric air mainly consists of oxygen and nitrogen. Consequently, the equation expressing the variation of air pressure with height can be written in the form

$$\begin{aligned} p(h) &= p_1(h) + p_2(h) \\ &= p_1(0) \exp[-m_1 gh/(kT)] + p_2(0) \exp[-m_2 gh/(kT)]. \end{aligned} \quad (10.12)$$

Thus [see (9.13)], the ratio of components, and hence the ratio of partial pressures, varies with height. However, the molar masses of oxygen and nitrogen are close, and this variation is insignificant. We mentioned it only to make the picture complete from the theoretical point of view. Actually, as regards the pressure, a gas mixture can be treated as a one-component gas with the average molecular mass

$$\langle m \rangle = (m_1 n_1 + m_2 n_2) / (n_1 + n_2).$$

Considering that $[m/(kT)] = \rho_0/p_0$, where ρ_0 and p_0 are the density and pressure at $h = 0$, the barometric formula can be written in the form

$$p(h) = p_0 \exp(-\rho_0 gh/p_0), \quad (10.13)$$

where p_0 on the Earth surface is taken equal to 101.325 kPa. Here we assume that the temperature does not vary with height. If we express the height in kilometers and assume that the temperature is equal to 0°C , the barometric formula can be written in another convenient form:

$$p(h) = p_0 \exp(-h/7.99). \quad (10.14)$$

In actual practice, however, the atmosphere is not stationary and the temperature decreases with height. This introduces considerable changes in the dependence of pressure on height. For certain average conditions corresponding to the mean pressure p_0 at the sea level and the mean temperature 15°C at the sea level up to the height 11 000 m (troposphere), the following expression is used as

the international barometric formula:

$$p(h) = 101.3 \left(1 - \frac{6.5h}{288} \right)^{5.255},$$

where p is the pressure in kPa and h is the height in km.

LIFTING FORCE. Let us find out how the lifting force acting in air on lighter-than-air aircrafts emerges. Suppose that we have a cylindrical rigid envelope whose contents are not important for us (Fig. 21a). For the sake of definiteness, we shall assume that the side walls of the cylinder of length L are vertical and that the upper and lower bases have the area S . If the concentration of a gas at the bottom of the cylinder is n_0 , its concentration at the top is equal to $n_1 = n_0 \exp[-mgL/(kT)] \approx n_0 [1 - mgL/(kT)]$. Consequently, the pressure on the cylinder bottom is $p_0 = n_0 kT$, which is larger than the downward pressure $p_1 = n_1 kT$ exerted on the top. The difference in the forces of pressure acting on the bottom and on the top creates the lifting force

$$F_{\text{lift}} = S(p_0 - p_1) = SLn_0 mg. \quad (10.15)$$

This force is equal to the weight of the gas which would occupy the volume of a body, just as it should be according to the Archimedes principle. The pressures acting on different parts of the body are shown in the figure by arrows. The resultant of these forces is the lifting force.

The mechanism of appearance of the lifting force acting on an aerostat is different. The aerostat has a soft envelope with a hole in the lower part, which contains a light gas. In order to analyze the emergence of the lifting force, we can represent the aerostat as a hollow cylinder without a bottom, whose lower part is filled with air and the upper part, by a lighter gas (Fig. 21b). At the level of contact between the light gas and air (dashed line) the pressure of air and the gas is the same and equal to the atmospheric pressure outside the cylinder. At this level, no force is acting on the side walls. With increasing height the pressure in the lighter gas decreases slower than in the heavier gas (air). Hence, above the level of contact between the light gas and air the pressure exerted by the light gas on the inner surface of the cylinder walls is higher than the air pressure on the outer surface of the walls. Consequently, all parts of the cylinder walls are subjected to forces directed outwards. In this case the lifting force is created due to a difference in pressure acting on the top. Let us determine this force assuming that the light gas fills the entire cylinder, i.e. the level of contact between the light gas and air coincides with the lower base (this is done

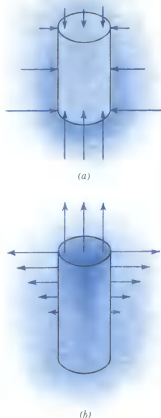


Fig. 21. Schematic diagram of forces resulting in the emergence of the Archimedes buoyant force (a) and the lifting force of an aerostat (b)

to make the comparison with the previous case easier). Then the pressures of air and the gas at the lower base are equal, and hence the concentration n_0 of the particles in these gases is the same. The concentrations of particles in the light gas (molecular mass m_1) and in air vary with height at different rates, and at the upper base we have

$$n_1 = n_0 \exp[-m_1 g L / (kT)], \quad n_2 = n_0 \exp[-m_2 g L / (kT)]. \quad (10.16)$$

Thus, the lifting force acting on the top of the cylinder is

$$F_{\text{lift}}^{(1)} = S(p_2 - p_1) = SkT(n_2 - n_1) = SLn_0g(m_2 - m_1), \quad (10.17)$$

i.e. it is smaller than the lifting force (10.15) acting on the closed cylinder. It is clear from (10.17) that the difference is equal to the weight of the light gas inside the cylinder. Formally, this result can be interpreted as follows: the lifting force acts on the cylinder in case (b) as well, but we must add the weight of the light gas inside the cylinder to the weight of the cylinder and its contents. Such an explanation leads to a correct result for the value of the lifting force but does not reflect correctly the physical aspect of emergence of the lifting force: in the first case the forces of pressure whose resultant creates the lifting force tend to compress the cylinder, while in the second case they tend to stretch it.

MEASUREMENT OF PRESSURE. Devices for measuring pressure are called manometers. The range of pressures to be measured in modern physical studies lies between 10^{-10} and 10^{11} Pa. Different methods are used for measuring pressures in different ranges of pressure.

Manometers can be divided into two categories. The first type includes those which measure the pressure as a quantity equal to the ratio of force to the surface area. They are absolute instruments and can be used as primary ones. Manometers of the second type measure a certain quantity associated with pressure rather than the pressure itself. Such manometers are called secondary.

In this book we do not aim at the description of the devices and the measuring techniques, which constitute the subject of laboratory practical works. Here, we shall only note general features of pressure measurement in different ranges.

In the low pressure region (below 100 Pa) secondary manometers are mainly used. Among them ionization and thermocouple gauges should be mentioned. The McLeod gauge has played a very important role in measuring low pressures. A gas whose pressure cannot be measured directly

because of its low value is compressed in it to directly measurable pressures. If we know the compression conditions, it is possible to find the initial pressure. Hence, McLeod's gauge directly measures the pressure although it is not an absolute instrument in the strict sense of the word. It is still being used in modern laboratories.

In the atmospheric pressure range liquid-column manometers are used. A manometer consists of a U-shaped tube with a high vacuum in one of the arms. Manometers for measuring the atmospheric pressure are called barometers. Liquid column manometers are primary devices which can measure the pressure with high accuracy.

Among the primary manometers for measuring high pressures, piston (free-piston) pressure gauges are the most important. In accordance with Pascal's principle, the pressure to be measured is transmitted to the fluid under the piston without loss. If the area of the piston is small, even at a very high pressure the force acting on the piston can be counterbalanced by another force whose magnitude is known. Thus, the pressure can be immediately determined.

Piston gauges are used for graduating secondary high-pressure gauges which include the widely used Bourdon gauge. This instrument is based on the following phenomenon: if the pressure of a fluid inside a curved tube is increased, the tube tends to straighten out, i.e. its ends move relative to one another. This relative motion of the tube ends is unambiguously connected with the pressure of the fluid inside the tube and can obviously be used for measuring pressure.

MOLAR AND SPECIFIC QUANTITIES. In molecular physics, the quantities are often referred to either a mole of a substance or its mass. In the former case they are called molar, and in the latter case specific quantities. Sometimes molar quantities are given the subscript "m". For example, the molar volume is written as $V_m = V/\nu$ (however, the molar gas constant R does not have this index). Specific quantities are denoted by the lower case of the same letter as the quantity itself, for instance, the specific volume $v = V/m$. The specific gas constant is denoted by $R_0 = R/M = \nu R/m$.

In many cases the formulas have the same form for molar and specific quantities. Hence, there is no need to write them twice or to overload them by indices. Therefore, in the cases where ambiguity is impossible, we shall omit the indices "m" for molar quantities in formulas which, depending on circumstances, can represent specific, molar, or simply arbitrary quantities. Otherwise, to avoid ambiguity, the nature of a quantity will be explicitly reflected by its notation.

?

1. Why is the expression "a mole of water" devoid of any meaning?
2. How many moles of oxygen atoms are contained in two moles of water molecules?
3. Do the internal degrees of freedom of a molecule affect the pressure?
4. Will the pressure of molecules on the wall increase or decrease if we take into account the finite dimensions of molecules?
5. How will the pressure change if we consider the forces of attraction acting among molecules?

By way of an example, let us consider the equation of state for an ideal gas. In the form (10.8), this equation describes the state of a gas with the molar mass M , having the mass m and occupying the volume V ; while in the form

$$pV = \nu RT \quad (\nu = m/M)$$

this is the equation for ν moles of a gas occupying the volume V . If we rewrite it in the form

$$pV_m = PT \quad (V_m = V/\nu),$$

we get the equation for a mole of m gas occupying the volume V_m , while in the form

$$pv = R_0 T \quad (v = V/m, \quad R_0 = R/M)$$

it refers to the specific volume of the gas. Thus, we must always bear in mind quantities which are being considered at the moment.

Example 10.1. An ideal gas contained in m cylinder of height z_0 and radius of the base r_0 is rotated around the cylinder axis at an angular velocity ω . Find the pressure of the gas on the side wall, if the total number of molecules in the cylinder is n and the gas temperature is T .

In the coordinate system fixed to the rotating cylinder, the gas molecules experience the inertial force $m\omega^2 r$ directed along the radius. It can be easily seen that this is a potential force, and hence the Boltzmann distribution can be applied to it if we assume that the gas is in the effective potential field $U = -m\omega^2 r^2/2$. Therefore, we can write the following expression for the number dn of molecules in the annular layer between r and $r + dr$ of height dz (z is the coordinate along the axis of rotation):

$$dn = A \exp [m\omega^2 r^2 / (2kT)] 2\pi r dr dz. \quad (10.18)$$

Here A is the normalization constant which can be found from the condition

$$n = \int_V dn, \quad (10.19)$$

where V is the volume of the cylinder. Substituting (10.18) into (10.19) and integrating, we obtain

$$\begin{aligned} n &= A\pi \int_0^{z_0} dz \int_0^{r_0} \exp \frac{m\omega^2 r^2}{2kT} d(r^2) \\ &= A\pi z_0 \frac{2kT}{m\omega^2} \left(\exp \frac{m\omega^2 r_0^2}{2kT} - 1 \right). \end{aligned} \quad (10.20)$$

Then the particle distribution along the radius of the cylinder is defined by

$$n_0(r) = \frac{n}{V} \frac{m\omega^2 r_0^2}{2kT} \frac{\exp[m\omega^2 r^2/(2kT)]}{\exp[m\omega^2 r_0^2/(2kT)] - 1}, \quad (10.21)$$

where $V = \pi r_0^2 z_0$.

The pressure on the lateral surface is

$$p(r_0) = n(r_0) kT. \quad (10.22)$$

Sec. 11. TEMPERATURE

The construction of an empirical temperature scale is considered and the dependence of temperature determined with the help of this scale on a thermometric body and a thermometric quantity is established. The temperature scale is considered with an ideal gas as a thermometric body. The International Practical Temperature Scale is described. The absolute nature of the zero kelvin is pointed out.

A THERMOMETRIC BODY AND A THERMOMETRIC QUANTITY. Temperature is a quantitative measure of the "degree of heating" of a body, which has a purely subjective meaning. We can define a more heated body and a less heated body. A more heated body is an object whose degree of heating decreases after a prolonged contact with another body which in this case is assumed, by definition, to be less heated. After this we could establish a scale of "degrees of heating" or "temperatures" in the same way as it was done while establishing the hardness scale. However, such a method of measuring "degree of heating" is inapplicable mainly because it is practically impossible to preserve the standards of invariable permanent "degree of heating" at all temperatures. The "degree of heating" of a body is determined from some characteristics of material bodies, which depend on the "degree of heating".

It is well known, for example, that the length of a solid depends on its "degree of heating"; in gases it is the pressure at a constant volume, and so on. The methods of measurement of length and pressure are well known. Hence, the measurement of the "degree of heating" is reduced to the measurement of a certain property of a body which varies with the degree of heating. The physical ground in this case is ensured by the validity of the statement that after a prolonged contact the degree of heating of the contacting bodies acquires the same value.

A body chosen for measuring the "degree of heating" is called a thermometric body, while the quantity used for determining the "degree of heating" is called a thermometric quantity.

TEMPERATURE SCALE. First of all, let us fix a thermometric body and denote by l a thermometric quantity.

For example, we can take a thermometric body in the form of a metallic rod of a certain length, this length being the thermometric quantity. Now, we must take for the start at least two typical "degrees of heating", or reference points which could be easily reproduced. The most easily determined and widely known are the "degree of heating" at which water boils under atmospheric pressure and that at which water freezes. These reference points are called the boiling point and freezing point of water. Suppose that the values of the thermometric quantity for the thermometric body at the boiling and freezing points are equal to l_2 and l_1 respectively. The numerical value of the quantity used to characterize the "degree of heating" of a body is called temperature. The temperature itself is not a thermometric quantity which is chosen as the basis for its measurement, and can be determined from the thermometric quantity as follows.

The temperature is expressed in degrees. The reference points can be assigned certain arbitrary temperatures. Suppose that the boiling point of water is assigned a temperature t_2 and the freezing point, t_1 . Then one degree of temperature can be defined as

$$1^\circ = (l_2 - l_1) / (t_2 - t_1).$$

The temperature of a thermometric body is the number determined according to the formula

$$t = t_1 + \frac{l_t - l_1}{1^\circ} = t_1 + \frac{l_t - l_1}{l_2 - l_1} (t_2 - t_1), \quad (11.2)$$

where l_t is the thermometric quantity for the "degree of heating" being measured. It should be emphasized once again that the "degree of heating" of a thermometric body is assumed to be the same as the "degree of heating" of any other body which is in contact with it for a sufficiently long time. Consequently, the quantity (11.2) is the temperature of the gas whose "degree of heating" is being measured.

Formulas (11.1) and (11.2) characterize a temperature scale. They have an unambiguous meaning only for a fixed thermometric body and a thermodynamic quantity.

Some of the temperature scales commonly used are the Celsius, Réaumur, and Fahrenheit scales which differ in the values of temperature ascribed to reference points. In the Celsius scale, $t_2 = 100$ and $t_1 = 0$; in the Réaumur scale $t_2 = 80$ and $t_1 = 0$, while in the Fahrenheit scale $t_2 = 212$ and

$t_1 = 32$. Consequently, the same "degree of heating" is characterized by different temperatures on these scales:

$$t_{\text{C}} = \frac{l_t - l_1}{l_2 - l_1} 100, \quad (11.3a)$$

$$t_{\text{R}} = (l_t - l_1) \cdot 80 / (l_2 - l_1), \quad (11.3b)$$

$$t_{\text{F}} = 32 + (l_t - l_1) \cdot 180 / (l_2 - l_1). \quad (11.3c)$$

In these formulas we presumed that the same thermometric body and thermometric quantity are used. Formulas (11.3) can be used to recalculate the temperature from one scale to another:

$$t_{\text{R}} = 0.8t_{\text{C}}, \quad t_{\text{F}} = 32 + 1.8t_{\text{C}}. \quad (11.4)$$

It should be noted that the magnitude of one degree is not the same for different scales.

Not all of these scales use the melting point of ice and boiling point of water as the reference points. The Dutch glass blower D. Fahrenheit (1686-1736) established a scale with the melting point of a mixture of ice with common salt as the first reference point. This point was assigned the temperature 0°F . The ice point was taken as the second reference point and ascribed the temperature 32°F . With such a choice, the steam point under normal conditions was equal to 212°F . The thermometric body was mercury or alcohol.

The French scientist R. Réaumur (1683-1757) proposed his scale in 1730. He chose the ice point as the initial reference point ($t_1 = 0^{\circ}\text{R}$) and defined a degree as a temperature increase causing the expansion of alcohol by 0.001 of its initial volume. On this scale, the steam point is $t_2 = 80^{\circ}\text{R}$.

The Swedish astronomer A. Celsius (1701-1744) proposed in 1742 his scale with the ice point and steam point as the reference points (however, instead of 0° and 100° accepted later, he assigned them the values 100 and 0°C).

THE DEPENDENCE OF TEMPERATURE ON THERMOMETRIC BODY AND THERMOMETRIC QUANTITY. Let us choose a thermometric body (for example, an iron wire) and a thermometric quantity (for example, its length), and construct some temperature scale (for example, Celsius' scale). Let us take another thermometric body (e.g., a copper wire) with the same thermometric quantity (its length) and also construct the Celsius scale. Let us measure the "degree of heating" of some body with the help of these thermometric bodies. Generally, we shall obtain different temperatures for the same "degree of heating". This is because the dependence of the length on the degree of heating is different for different bodies. Hence, the value of temperature on the same

temperature scale depends on thermometric body. If we fix the thermometric body and the temperature scale but vary the thermometric quantity used for measuring the temperature, we shall also obtain, generally speaking, different temperatures for the same degree of heating. Consequently, temperature depends on the choice of a thermometric body.

This was established experimentally at the beginning of 19th century by the English chemist H. Davy (1778-1829) who showed that thermometers using different liquids as thermometric bodies give different temperatures in the interval between 0 and 100 °C.

For this reason, it is necessary to agree once and for all upon a choice of a thermometric body and a thermometric quantity. This choice can in principle be arbitrary, but actually, while working out an agreement, we must take into account the convenience and precision of measurements, preservation of the thermometric body and the thermometric quantity, reproducibility of the thermometric body and the results of measurement, the interval of "degrees of heating" for which the thermometric body can be used, and so on. If we consider all these conditions, the arbitrariness in the choice of thermometric body is practically eliminated, and we ultimately arrive at an ideal gas as the thermometric body.

THERMODYNAMIC TEMPERATURE SCALE. Even a few requirements to a thermometric body listed above suggest the idea that an ideal gas must be taken as the thermometric body. The equation (10.6a) of state for an ideal gas permits to take as thermometric quantity either p or V which can be measured to a high accuracy. The reproducibility of this thermometric body is in principle absolute, as well as preservability and invariability. Its only drawback is that it does not exist in nature. However, this drawback is not of principle importance since physicists always operate with abstract idealized models, and it is always possible to find out to which extent the real models approach the ideal ones and to reveal the difference between them.

We can choose a gas and after analyzing its behaviour determine to which extent it is close to an ideal gas. Experiments show that rarefied gases are very close to ideal, and therefore we can directly take them as thermometric bodies. Equation (10.6a) contains three variables, hence we can say that this equation contains the definition of temperature and two laws which are usually assumed to be the Boyle law and the law of volumes (Gay-Lussac's law). Therefore, although this equation forms the basis of the

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Temperature is not a thermometric quantity. For this reason, its measurement resembles the measurement of altitude with the help of a barometer, where depending on circumstances this can be done either by measuring pressure or allowing the barometer to fall to the ground, and by measuring the time of the fall. However, there is no other way of doing this.

For a fixed scale and reference points, the temperature depends on the choice of a thermometric body and thermometric quantity.

definition of temperature, it can be used to find out how close a given thermometric body is to an ideal gas.

Either p or V can be taken as a thermometric quantity. If we choose V as such a quantity, Gay-Lussac's law ceases to be a law and becomes a corollary of the adopted definition of temperature. In this case the second independent law for ideal gases (besides the Boyle law) is the Charles law $p_1/p_2 = T_1/T_2$.

For reference points we can take the ice point and the steam point whose temperatures will be denoted by T_1 and T_2 . By definition, a degree of temperature can be chosen in such a way that the difference between the indicated temperatures be equal to 100, i.e. $T_2 - T_1 = 100$. For the thermometric quantity we shall take pressure. We can measure experimentally the pressure p_2 of a certain mass of gas close to ideal at the steam point and the pressure p_1 at the ice point. Suppose that the ratio of the experimentally measured quantities is 1.3661. Hence, we have two equations for calculating T_1 and T_2 : $T_2 - T_1 = 100$ K and $T_2/T_1 = 1.3661$, whose solution yields $T_1 = 273.15$ K and $T_2 = 373.15$ K. Thus, the temperature scale is fixed completely.

However, such an introduction of a temperature scale is not quite satisfactory. As a matter of fact, the steam point and the ice point depend on pressure which must be additionally fixed in the definition. Moreover, the boiling and freezing points are fixed with insufficient accuracy. For this reason, in the International System the temperature scale is defined by a single reference point, viz. the triple point of water (see Sec. 47). By definition, the temperature corresponding to the triple point of water is taken equal to 273.16 K. The unit of temperature is defined as $1/273.16$ of the temperature interval between the triple point and the absolute zero which, however, is not a reference point but just the temperature 273.16 K below the triple point of water.

Taking an ideal gas as a thermometric body, we can determine temperature by the formula

$$T = \frac{273.16}{p_0} p, \quad (11.5)$$

where p_0 is the gas pressure at the temperature corresponding to the triple point of water and p is its pressure at the temperature being measured. The volume of the gas must be constant during measurements.

The temperature scale determined above is called the absolute thermodynamic temperature scale.

Since Eq. (11.5) is based on the ideal gas laws, the quantity

T defined by this formula coincides with T introduced in (8.15) as notation. Hence, the temperature denoted by T in the previous discussion is the absolute thermodynamic temperature.

It is called "thermodynamic" since it can be derived from purely thermodynamic calculations on the basis of the second law of thermodynamics. Formally, we had no grounds to call it thermodynamic since a thermodynamic analysis of the problem has not been made so far. To avoid excessive terminology it is expedient, however, to do it now putting off its substantiation till later.

THERMOMETERS. A rarefied gas is a real thermometric body that is closest to an ideal gas. Thermometers on the basis of rarefied gases are called gas thermometers. The thermodynamic temperature scale can be realized with their help in a wide temperature range from several kelvins to more than a thousand kelvins. For this reason, the Bureau of Standards uses gas thermometers as primary standards in this temperature range. The thermometric quantity in gas thermometers is the pressure. These thermometers are very cumbersome and difficult to use. For this reason, they are used only to graduate secondary thermometers employed in scientific investigations, in industry, and so on. The most common secondary thermometers are liquid-filled thermometers (for example, alcohol and mercury thermometers), resistance thermometers, and thermocouples. Liquid-filled thermometers are used in the temperature range between -200 and 600°C . For example, pentane thermometers operate between -200 and 20°C , while mercury thermometers, from -38.87 to 600°C .

Resistance thermometers are based on the dependence of the ohmic resistance of a conductor on temperature. Among them, platinum resistance thermometers have the widest range of temperatures accessible for measurements (from -200 to 1100°C). The International Bureau of Weights and Measures recommended the platinum thermometer as a standard for reproducing temperatures in the range from -190 to 660°C . Copper resistance thermometer can be used for the temperature interval from -20 to 100°C . Resistance thermometers can be used for measuring low temperatures (bronze and graphite thermometers). Semiconductors can also be used as materials for resistance thermometers. Their resistance decreases and not increases with temperature, while the rate of temperature variation of resistance is an order of magnitude higher than for metals. This property is used for manufacturing very sensitive semiconductor thermometers called thermistors.

Physical phenomena occurring in thermocouples will be considered in Sec. 56. Temperature measurements with the help of thermocouples are reduced to measuring the potential difference. With these instruments, temperature can be measured over a wide range. For example, a platinum/platinum-rhodium thermocouple can be used in the interval from 0 to 1700°C, and chromel/alumel thermocouple, from -200 to 1350°C.

At very high temperatures, materials melt and the types of thermometers described above are inapplicable. In this case, the body whose temperature is to be measured is taken as the thermometric body, while the thermometric quantity is the electromagnetic energy emitted by it. The laws of radiation are well known and can be used for determining the temperature of a body from its radiation. The International Bureau of Weights and Measures has established the thermodynamic scale for temperature above 1063°C just on the basis of the laws of radiation. The instruments used for measuring radiant energy are called pyrometers.

At very low temperatures (≈ 1 K) conventional methods of measuring temperatures are also inapplicable, since the temperatures of bodies in contact level out in this case very slowly, and, in addition, the ordinary thermometric quantities are "non-operative" (for example, pressure becomes extremely low, and resistance is practically independent of temperature). In these conditions also the body itself is taken as a thermodynamic body while the characteristics of its properties, e.g. magnetic, are used as thermometric quantities. The problem of measuring temperature is closely linked with the investigation of variation of properties of a substance with temperature.

On the whole, the design of thermometers for various temperature intervals and their calibration is a complex scientific and technical problem, where physical laws established for appropriate temperature ranges are employed.

INTERNATIONAL PRACTICAL TEMPERATURE SCALE.

This scale was established for calibrating in comparatively simple ways scientific and technical instruments and, at the same time, for reproducing the thermodynamic temperature scale with the highest possible accuracy. The units of temperature are degrees Kelvin or Celsius depending on the reference point of temperature. The temperature scale is constantly being refined in accordance with the results of researches and advances in measuring technique. This scale employs as the primary fixed points the readily reproducible points to which definite temperatures are ascribed. They are used for graduating standard thermometers which are

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1. Which body is chosen as the thermometric body for the absolute thermodynamic temperature scale? What are the merits of such a choice?
2. How many reference points are used to define the absolute thermodynamic temperature scale in SI?
3. List the fixed primary points for the International Practical Temperature Scale.
4. Which thermometers and what methods are used for measuring temperature in various intervals?

Table 1
Primary Fixed Points on the International Temperature Scale
(under standard pressure $p = 101.325 \text{ kPa}$)

Fixed points	$T \text{ (K)}$	$t \text{ (}^\circ\text{C)}$
Triple point of hydrogen	13.81	-259.34
Boiling point of oxygen	90.188	-182.962
Triple point of water	273.16	0.01
Boiling point of water	373.15	100.0
Melting point of zinc	692.73	419.58
Melting point of silver	1235.08	961.93
Melting point of gold	1337.58	1064.43

suitable due to their physical properties for measuring temperature in appropriate intervals. Between the primary points, the temperature scale is established with the help of interpolation formulas according to which the temperature is found from the readings of thermometers adopted as $\equiv$ standard.

The scale constructed in this way is on the whole in very good accord with the thermodynamic temperature scale at the reference points and is sufficiently accurate for all other points.

The temperature corresponding to some primary fixed points of the International Temperature Scale is given in Table 1

RELATION BETWEEN THE THERMODYNAMIC AND CELSIUS SCALES. The Celsius scale is obtained from the fact that the freezing point of water under the pressure of $1.013 \times 10^5 \text{ Pa}$ is equal to 0°C , and one degree Celsius is equal to one degree Kelvin. On the thermodynamic scale, the ice point under these conditions is 273.15 K . Thus, by definition, the temperature t on the Celsius scale is given by

$$t = T - 273.15. \quad (11.6)$$

ZERO KELVIN. It follows from the definition (11.5) that the temperature cannot change sign, since the existence of a negative pressure of an ideal gas is ruled out. As the reference temperature is assumed to be positive by definition, thermodynamic temperature cannot take negative values (this question is treated in Sec. 21).

The existence of states with zero thermodynamic temperature is not excluded by these considerations. However, an analysis of various processes shows that zero kelvin cannot be attained, although the possibility of



The International Practical Temperature Scale is defined in such a way that measuring instruments can be easily calibrated and thermodynamic temperature scale reproduced quite exactly.

Thermodynamic temperature cannot be negative.

Zero thermodynamic temperature is unattainable, although the possibility of approaching it however closely is not excluded.

approaching it however closely is not excluded. The statement about the unattainability of zero kelvin is formulated in thermodynamics as an independent postulate called the **third law of thermodynamics**.

It can be seen from Eq. (8.18) that $\langle mv^2/2 \rangle = 3kT/2$, and hence at 0 K the kinetic energy must vanish. In particular, thermal vibrations of atoms at the lattice sites must cease. This, however, is in contradiction to the basic postulates of quantum mechanics.

According to Heisenberg's uncertainty relations, a decrease in the momentum of particles is inevitably accompanied by an increase in the uncertainty in their coordinates. Consequently, the assumption that the atoms have stopped vibrating at the crystal lattice sites is equivalent to the statement that the lattice has ceased to exist. On the other hand, a direct solution of the quantum-mechanical problem about atomic vibrations at the lattice sites shows that the energy of atomic vibrations can never become lower than a certain minimum value. The vibrations corresponding to this energy are called zero-point vibrations. The existence of zero-point vibrations in crystals was confirmed in experiments.

Example 11.1. A constant-volume helium thermometer employs pressure as a thermometric quantity. The values $t'_1 = 0$ and $t'_2 = 100$ correspond to the ice point and steam point. Estimate the error introduced during measurements with helium thermometer if it is established experimentally that the helium pressure in a thermometer with volume $V = 5000 \text{ cm}^3$ is sufficiently accurately described by the equation

$$p = \frac{rT}{V} - \frac{a}{TV^2} \quad (T = 273 + t), \quad (11.7)$$

where $r = 2 \times 10^7$, $a = 8.4 \times 10^9$, and p is measured in arbitrary units not important for the problem.

Taking helium as a thermometric body and pressure as a thermometric quantity of constant volume, we define temperature as it was done in (11.3a):

$$t' = \frac{p - p_0}{p_{100} - p_0} \cdot 100. \quad (11.8)$$

Rewriting this equation as

$$t'(p_{100} - p_0) = 100(p - p_0),$$

we find that

$$t' \left[100 \frac{r}{V} - \frac{a}{V^2} \left(\frac{1}{373} - \frac{1}{273} \right) \right] \\ = 100 \left[t \frac{r}{V} - \frac{a}{V^2} \left(\frac{1}{273+t} - \frac{1}{273} \right) \right]$$

or

$$t'(1 + A/373) = t[1 + A/(273 + t)]; \quad A = a/(273rV). \quad (11.9)$$

This equation shows that at $t_1 = 0^\circ\text{C}$ and $t_2 = 100^\circ\text{C}$ the helium thermometer shows $t'_1 = 0$ and $t'_2 = 100$, i.e. at this points the readings of the thermometer are exact. At other points its readings differ from accurate values. Considering that $A = 8.44 \times 10^9 / (2 \times 10^7 \times 273 \times 5 \times 10^3) = 3.1 \times 10^{-4}$, we can represent t' from (11.9) in the form

$$t' \simeq t[1 + A/(273 + t)](1 - A/273) \\ \simeq t[1 + A/(273 + t) - A/273 + \dots],$$

whence

$$t' - t = t \frac{A(100 - t)}{373(273 + t)} = t \cdot 8.3 \cdot 10^{-7} \frac{100 - t}{273 + t},$$

i.e. the thermometer is sufficiently accurate. For example, at $t = 50$ the difference $t' - t = 6.4 \times 10^{-6}$, while at $t = 200$, $t' - t = -3.5 \times 10^{-5}$.

Sec. 12. DISTRIBUTION OF ENERGY AMONG THE DEGREES OF FREEDOM

The principle of equipartition of energy is proved and the conditions for its applicability to complex particles with internal degrees of freedom are revealed.

THE NUMBER OF DEGREES OF FREEDOM. This quantity is defined as the number of independent variables which determine the state of a system. In order to completely describe the energy state of motion of a material point at a certain moment, we must assign to it three velocity components for determining the kinetic energy and three coordinates for the potential energy, i.e. six variables in total. In the dynamics analysis of the motion of an individual particle, these variables are not independent, since having solved the equation of motion, we can express the coordinates as functions of time, while the velocities are expressed as time derivatives of the coordinates. If, however, a particle becomes a part of a statistical system, such an approach is impossible, and we must consider the particle with all its six degrees of freedom.

A statistical system comprising n point particles has $6n$ degrees of freedom of which $3n$ determine the kinetic energy of the system and $3n$, the potential energy (if the system is in an external potential field or if its particles interact with each other through potential forces). For an ideal gas it is assumed that this type of interaction does not exist.

THE $6n$ -DIMENSIONAL PHASE SPACE METHOD. Two methods are used for describing many-particle systems (see Sec. 8). The problem can be reduced to the analysis of the motion of the totality of n particles in the $6n$ -dimensional phase space of the variables x, y, z, p_x, p_y, p_z . This method has been used so far, since it provides a more graphic picture. We shall turn, however, to a different method to prove the principle of equipartition of energy among the degrees of freedom.

In this case, in the Gibbs distribution (7.5) ϵ_α should be treated as the energy of a certain state of a system of n particles. The entire system is submerged into a very large system with temperature T . Here the canonical ensemble will be a large number of such systems containing n particles each.

The energy ϵ_α of the system is the sum of the kinetic energies of the particles plus the sum of their potential energies. A certain specific state of the system is characterized by the values of all momentum components and coordinates of all particles constituting the system, i.e. by $6n$ variables.

Hence we can assume that the state of a system corresponds to a point in the $6n$ -dimensional phase space. Essentially, it is as difficult to imagine the $6n$ -dimensional space as a six-dimensional one since in both cases the visual representation such as we have for a three-dimensional space is impossible. For this reason, the two-dimensional phase space will be the initial space described by one coordinate and one momentum. Such a space can be shown graphically. Then, we can go over to a four-dimensional, six-dimensional, and so on, phase space, all these multidimensional spaces being equally abstract for our imagination. The elementary phase volume in a $6n$ -dimensional space is expressed as

$$dx_1 dy_1 dz_1 dp_{x1} dp_{y1} dp_{z1} \dots dx_n dy_n dz_n dp_{xn} dp_{yn} dp_{zn}, \quad (12.1)$$

i.e. the product of phase volumes occupied by each particle of the system. In order to simplify the notation, we shall denote the product of all differentials of coordinates by $\{dx\}$ and of momenta by $\{dp\}$, i.e. an element of the phase volume will be written as $\{dx\} \{dp\}$.

According to (4.1), each particle in its phase space occupies the volume $(2\pi\hbar)^3$. Consequently, n particles in the $6n$ -dimensional space occupy the volume $(2\pi\hbar)^{3n}$, and hence instead of (8.1) we have

$$d\Gamma = \{dx\} \{dp\} / (2\pi\hbar)^{3n}. \quad (12.2)$$

Instead of formula (8.2), for the probability that particles can be found in the volume element $\{dx\} \{dp\}$ of the $6n$ -dimensional space, we get

$$d\mathcal{P} = A \exp(-\beta \varepsilon_a) d\Gamma. \quad (12.3)$$

As before, the constant A is determined from the normalization conditions. To calculate the probability that a system of particles has a given energy ε_a , we must integrate (12.3) over all elements of the phase space, that correspond to the energy ε_a . Thus we shall take into account the contribution to the probability from all states described by the same energy ε_a . So, the method of the $6n$ -dimensional phase space employs the same concepts and methods that were used more graphically in Secs. 7-9 when we introduced the six-dimensional phase space. The procedure for calculating the mean values will also be similar.

CALCULATION OF THE MEAN VALUE CORRESPONDING TO ONE DEGREE OF FREEDOM. Let us calculate the mean value of the kinetic energy corresponding to the x -component of the i th particle:

$$\left\langle \frac{m_i v_{xi}^2}{2} \right\rangle = \left\langle \frac{p_{xi}^2}{2m_i} \right\rangle. \quad (12.4)$$

Here the mass of the particle is marked with the subscript i since the masses of the particles can in general be different. The energy of the system can be written as

$$\varepsilon_a = p_{xi}^2 / (2m_i) + \varepsilon'_a \quad (12.5)$$

where ε'_a is the total energy of the system less $p_{xi}^2 / (2m_i)$, whose mean value is to be determined. The volume element of the phase space can be written in the form

$$\{dx\} \cdot \{dp\} = \{dx\} dp_{xi} \{dp\}', \quad (12.6)$$

where $\{dp\}'$ is the product of all differentials of momenta of particles except the differential dp_{xi} which is factorized from the product: $\{dp\} = dp_{xi} \{dp\}'$. The value of the quantity (12.4) is determined by the mean value formula:

$$\begin{aligned} \left\langle \frac{p_{xi}^2}{2m_i} \right\rangle &= \frac{\int \exp[-\beta p_{xi}^2/(2m_i)] \frac{p_{xi}^2}{2m_i} dp_{xi} \int \exp(-\beta \epsilon_a') \{dx\} \{dp\}'}{\int \exp[-\beta p_{xi}^2/(2m_i)] dp_{xi} \int \exp(-\beta \epsilon_a') \{dx\} \{dp\}'} \quad (12.7) \end{aligned}$$

where the denominator is the quantity reciprocal to the normalization constant A , that emerges due to a normalization of (12.3) to unity. The integrals in the numerator and denominator of (12.7) over all variables excluding p_{xi} cancel out, after which we have

$$\begin{aligned} \left\langle \frac{p_{xi}^2}{2m_i} \right\rangle &= \frac{\int_{-\infty}^{\infty} \exp[-\beta p_{xi}^2/(2m_i)] [p_{xi}^2/(2m_i)] dp_{xi}}{\int_{-\infty}^{\infty} \exp[-\beta p_{xi}^2/(2m_i)] dp_{xi}} \\ &= -\frac{\partial}{\partial \beta} \ln \int_{-\infty}^{\infty} \exp\left(-\frac{\beta p_{xi}^2}{2m_i}\right) dp_{xi}. \quad (12.8) \end{aligned}$$

We have already used such a representation of the mean value in (7.15). The integral similar to the one under the logarithm sign in (12.8) is known from (8.8), hence

$$\left\langle \frac{p_{xi}^2}{2m_i} \right\rangle = \frac{1}{2\beta} = \frac{kT}{2}. \quad (12.9)$$

! The law of equipartition of energy concerns the mean energy per degree of freedom. At a certain instant of time, the energy associated with a given degree of freedom may acquire various values which in general differ from the energies corresponding to other degrees of freedom. The energies connected with different degrees of freedom are equal only when averaged, over a sufficiently long interval of time. By the ergodic hypothesis, this also means that the values of energy corresponding to specific degrees of freedom, averaged over the ensemble, are also equal to each other.

This formula expresses a very important statement: in a system consisting of n particles, each degree of freedom contributing to the kinetic energy of the system has the same energy equal to $kT/2$. It should be emphasized once again that this conclusion is valid for the case when the masses of particles are different. Using (12.9), we can write the following expression for the total kinetic energy of the system:

$$W = 3n kT/2, \quad (12.10)$$

since the system has $3n$ degrees of freedom contributing to the kinetic energy.

There is no general rule of this type for the potential energy of different degrees of freedom. However, if the potential energy has a specific but very important and frequently encountered form, there exists a certain rule for it, which we shall now prove.

COMPLEX PARTICLES WITH MANY DEGREES OF FREEDOM. Suppose that each of n particles of a system is

not a point particle but consists of several point particles coupled into a single entity by some forces which, without any loss of generality, can be considered potential forces, since otherwise the energy of complex particles would not be conserved and they cannot be assumed to exist in stationary conditions. So, the system of n complex particles is transformed into a system of N particles, when N represents the number of all point particles comprising n complex particles. In this case we need not assume that all n complex particles are identical and consist of the same number of point particles. It follows from the derivation of the Gibbs canonical distribution (7.5) that it can be applied to an ensemble of N point particles.

Let us now consider one of the complex particles. Suppose that it consists of s point particles. The motion of the complex particle as a whole is characterized by the motion of its constituent particles, i.e. it has $6s$ degrees of freedom. However, it is expedient to represent these $6s$ degrees of freedom in a more convenient form, as it was done in the case of a rigid body with six degrees of freedom. If the point particles are fixed in the centre of mass coordinate system for a complex particle, the complex particle behaves as a set of motions of the centre of mass and rotations around it. The formula for describing the kinetic energy of the particle is well known. The only difference between this complex particle and a rigid body is that the rotation is not possible about all principal central axes. For example, if a complex particle consists of two point particles, the rotation about the axis passing through the point particles is impossible. The formula for kinetic energy contains the term corresponding to this axis, but the moment of inertia J with respect to this axis is equal to zero. Hence, the kinetic energy of a complex particle, associated with its translatory motion and rotation, can be written in the form

$$W_0 = m_i v_i^2 / 2 + (J_1 \omega_1^2 + J_2 \omega_2^2 + J_3 \omega_3^2) / 2, \quad (12.11)$$

where m_i is the mass of a complex particle, equal to the sum of the masses of point particles constituting it, v_i is the velocity of its centre of mass, J_1 , J_2 , J_3 , and ω_1 , ω_2 , ω_3 are the moments of inertia and angular velocities of rotation of the complex particle, corresponding to its principal central axes.

The total energy of a complex particle consists not only of its kinetic energy (12.11). The point particles constituting it are not at rest but rather move in the vicinity of their equilibrium positions. These deviations are small, and hence

the motion of particles can be reduced to vibrations about equilibrium positions, i.e. the motion of linear oscillators. Let us consider one of the vibrational motions of the j th point particle about its equilibrium position. We denote its deviation from the equilibrium position by ξ_{ij} and the velocity by η_{ij} . Its kinetic and potential energies are respectively given by

$$W_{ij} = m_{ij}\eta_{ij}^2/2; \quad U_{ij} = k_{ij}\xi_{ij}^2/2. \quad (12.12)$$

Here the first index in the subscript denotes the number of a complex particle, while the second labels the point particle inside it. These energies are added to the energy (12.11) of motion of the centre of mass and rotation. Hence the total energy of the i th particle can be represented as

$$\begin{aligned} \varepsilon_{ix} = & \frac{1}{2}m_i v_i^2 + \frac{1}{2}(J_{i1}\omega_{i1}^2 + J_{i2}\omega_{i2}^2 + J_{i3}\omega_{i3}^2) \\ & + \sum_j \frac{m_{ij}\eta_{ij}^2}{2} + \sum_j \frac{k_{ij}\xi_{ij}^2}{2} + U_i(x_i, y_i, z_i), \end{aligned} \quad (12.13)$$

where $U_i(x_i, y_i, z_i)$ is the potential energy of the complex particle as a whole in external fields. We did not explicitly indicate how many values the index j assumes in the sums of (12.13). It assumes as many values as is required to exhaust all degrees of freedom of the complex particle. There is no need to specify this number at the moment. The fact that the kinetic energy in (12.13) is indeed represented as the sum of the squares of velocities can be proved as follows.

Suppose that $\mathbf{r}_{ij}$ is the radius vector of the j th point particle in the centre of mass system. By definition of the centre of mass,

$$\sum_j m_{ij}\mathbf{r}_{ij} = 0. \quad (12.14)$$

The velocity of the j th particle in the centre of mass system is $\mathbf{v}_{ij} = \dot{\mathbf{r}}_{ij}$, and hence the following equality must hold in accordance with (12.14):

$$\sum_j m_{ij}\mathbf{v}_{ij} = 0. \quad (12.15)$$

The total kinetic energy of a complex particle is

$$\begin{aligned} W &= \sum_j \frac{m_{ij}(\mathbf{v}_i + \mathbf{v}_{ij})^2}{2} = \sum_j \frac{m_{ij}v_i^2}{2} + 2 \sum_j \frac{m_{ij}(\mathbf{v}_i \cdot \mathbf{v}_{ij})}{2} + \sum_j \frac{m_{ij}v_{ij}^2}{2} \\ &= \frac{v_i^2}{2} \sum_j m_{ij} + 2 \left(\mathbf{v}_i \cdot \sum_j m_{ij}\mathbf{v}_{ij} \right) + \sum_j \frac{m_{ij}v_{ij}^2}{2}, \end{aligned} \quad (12.16)$$

where $\mathbf{v}_i$ is the velocity of the centre of mass.

The second term in this equation is equal to zero (see (12.15)), while the first term is the kinetic energy $m_i v_{ij}^2/2$ due to the motion of the centre of mass. The velocity v_{ij} can be decomposed into two components: the velocity $\omega \times r'_{ij}$ of rotation of the complex particle as a whole around an instantaneous axis of rotation at the angular velocity ω and the velocity v''_{ij} of vibrational motion:

$$v_{ij} = \omega \times r'_{ij} + v''_{ij}, \quad (12.17)$$

whence

$$\sum_j \frac{m_{ij} v_{ij}^2}{2} = \sum_j \frac{m_{ij}}{2} (\omega \times r'_{ij})^2 + 2 \sum_j \frac{m_{ij}}{2} (\omega \times r'_{ij}) \cdot v''_{ij} + \sum_j \frac{m_{ij} v_{ij}''^2}{2}. \quad (12.18)$$

The first term in this formula can be transformed to the term containing the squares of the angular velocity components in (12.13), the second term vanishes since the velocities $\omega \times r'_{ij}$ and v''_{ij} are mutually perpendicular, while the third term written for the projections on the coordinate axes in (12.13) just gives components containing η_{ij}^2 . As regards the terms containing ξ_{ij}^2 , their presence is obvious from the form of the potential energy for an oscillator and the additivity of the potential energy. Thus, we have completely justified the expression (12.13) for the energy of a complex particle.

The volume (12.1) of an elementary cell of the phase space must now include the degrees of freedom of all the particles. Hence, the set of differentials $\{dx\} \{dp\}$ must comprise the coordinates and momenta of the centres of mass of complex particles, the differentials $d\xi_{ij}$ of the variables taking into account the internal potential energy of a complex particle associated with the corresponding degree of freedom, the differentials $d\eta_{ij}$ of the variables responsible for the kinetic energy of the internal degrees of freedom of the particle, as well as the differentials $d\omega_{i1}$, $d\omega_{i2}$, and $d\omega_{i3}$ which take into consideration the rotational energy of the complex particle. Strictly speaking, the differentials $d\eta_{ij}$ and $d\omega_{i\gamma}$ ($\gamma = 1, 2, 3$) must be expressed as variables having the dimensions of momentum, which is not difficult. However, we need not do this while calculating the mean values because the factors appearing in this case cancel out.

PRINCIPLE OF THE EQUIPARTITION OF ENERGY AMONG THE DEGREES OF FREEDOM. We can now find the mean energy per degree of freedom of a particle by the formulas for the mean values and those similar to (12.7). Let us determine, for example, the mean energy per rotational degree of freedom $i\gamma$, i.e. per rotational degree of freedom of

the i th particle with the component γ :

$$\begin{aligned} \left\langle \frac{1}{2} J_{i\gamma} \omega_{i\gamma}^2 \right\rangle &= \frac{\int [J_{i\gamma} \omega_{i\gamma}^2 \exp(-\beta J_{i\gamma} \omega_{i\gamma}^2 / 2)] d\omega_{i\gamma} \int \exp(-\beta \epsilon_a) \{dx\} \{dp\}'}{\int \exp(-\beta J_{i\gamma} \omega_{i\gamma}^2 / 2) d\omega_{i\gamma} \int \exp(-\beta \epsilon_a) \{dx\} \{dp\}'}, \end{aligned} \quad (12.19)$$

where $\{dp\}'$ is the totality of all differentials excluding the one appearing in the first integral. Calculating in the same way as in (12.7), we get

$$\left\langle \frac{1}{2} J_{i\gamma} \omega_{i\gamma}^2 \right\rangle = \frac{1}{2\beta} = \frac{1}{2} kT. \quad (12.20)$$

Similarly, we can find the expressions for the mean kinetic and mean potential energies per vibrational degree of freedom:

$$\left\langle \frac{m_{ij} \eta_{ij}^2}{2} \right\rangle = \frac{1}{2} kT, \quad \left\langle \frac{k_{ij} \xi_{ij}^2}{2} \right\rangle = \frac{1}{2} kT. \quad (12.21)$$

The mean kinetic energy per degree of freedom in the motion of the centre of mass of a complex particle is calculated in absolutely the same way as in (12.7) and is equal to $kT/2$. Thus we have proved that the energy corresponding to a degree of freedom of a statistical system is the same and equal to $kT/2$. This statement is called the principle of equipartition of energy among the degrees of freedom. It is appropriate to emphasize once more that this does not refer to the potential energy of particles in external fields, where it may have a mean value different from $kT/2$.

The law of equipartition of energy is of great importance. Due to this law, the mixture of ideal gases which had the same initial temperature before mixing has a temperature equal to that of the components being mixed, while the pressure of the mixture thus obtained obeys the Dalton law.

Example 12.1. Calculate the partition function (7.16) for a monoatomic gas.

The energy ϵ_a in the exponent of (7.16) is equal to the sum of the kinetic energies of n particles under consideration:

$$\epsilon_a = [1/(2m)](p_{1a}^2 + p_{2a}^2 + \dots + p_{na}^2). \quad (12.22)$$

where the first subscript on p numbers the particles, while the index α characterizes different states of the system of n particles, and m is the mass of particles. The potential energy of the particles is equal to zero, and the internal degrees of freedom are absent.

Let us go over from summation to integration in (7.16). For this, we multiply each term in (7.16) by $d\Gamma$ given by (12.2) and integrate over Γ . We get the statistical integral

$$Z = \int_{\Gamma} \exp [-(p_1^2 + p_2^2 + \dots + p_n^2)/(2mkT)] d\Gamma, \quad (12.23)$$

where Γ is the domain of integration over the entire phase space Γ minus physically equivalent points of this space.

Integration over Γ presumes the integration over the set of spatial variables $\{x\}$ and momentum variables $\{p\}$. Since the integrand in (12.23) does not contain spatial variables, the integration over $\{x\}$ gives the factor V^n , where V is the volume occupied by the gas. While integrating over $\{p\}$, we must exclude physically equivalent states. This means that the transpositions of particles must not be taken into account, i.e. we must integrate over the entire domain of $\{p\}$ and divide the result by $n!$:

$$Z = \frac{V^n}{(2\pi\hbar)^{3n}n!} \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} \exp \left[-\frac{p_1^2 + p_2^2 + \dots + p_n^2}{2mkT} \right] \{dp\}. \quad (12.24a)$$

The integrals with respect to each of the variables p_x, p_y, p_z in (12.24a) are identical and equal to

$$\int_{-\infty}^{\infty} \exp [-p^2/(2mkT)] dp = (2\pi mkT)^{1/2},$$

whence

$$\begin{aligned} & \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} \exp [-(p_1^2 + p_2^2 + \dots + p_n^2)/(2mkT)] \{dp\} \\ &= \left\{ \int_{-\infty}^{\infty} \exp [-p^2/(2mkT)] dp \right\}^{3n} = (2\pi mkT)^{3n/2}. \end{aligned} \quad (12.24b)$$

Taking into account the Stirling formula (5.11), we finally get for the statistical integral (12.24a)

$$Z = \frac{e^n V^n}{(2\pi\hbar)^{3n} n^n} (2\pi mkT)^{3n/2}. \quad (12.25)$$

If we know the partition function (statistical integral), we can determine the thermodynamic functions and quantities characterizing the system. Examples of this type of

calculations will be considered below. Let us calculate the mean energy of a monoatomic gas with the help of formula (7.15). Taking logarithms of both sides of (12.25), we find

$$\ln Z = +n \left\{ \ln \left[\frac{(2\pi mkT)^{3/2} V}{n (2\pi\hbar)^3} \right] + 1 \right\}. \quad (12.26)$$

Considering that $\beta = 1/(kT)$ and using formula (7.15), we obtain from (12.26)

$$\langle \varepsilon \rangle = - \frac{\partial}{\partial \beta} \left[n \ln \frac{1}{\beta^{3/2}} \right] = \frac{3}{2} n \frac{\partial}{\partial \beta} (\ln \beta) = \frac{3}{2} nkT. \quad (12.27)$$

This is just the mean energy of a gas consisting of n similar monoatomic molecules. The energy per molecule is $\langle \varepsilon \rangle/n = (3/2)kT$, while the energy per degree of freedom of translational motion of a molecule is equal to $(1/2)kT$, in accordance with the law of equipartition of energy.

Sec. 13. BROWNIAN MOVEMENT

The elementary theory of random wandering is exposed by using the Brownian movement as an example. The experimental determination of Boltzmann's constant on the basis of the results of observation of the Brownian movement is discussed. Rotational Brownian movement and manifestations of this movement in macroscopic phenomena are considered.

ESSENCE. Tiny particles held in suspension in a liquid are seen through a microscope as performing unceasing vibrations. These vibrations do not change with time and may continue indefinitely. They can be observed in liquid inclusions of minerals formed many thousands of years ago. This movement is called Brownian after the English botanist R. Brown who discovered it in 1827.

The molecular-kinetic account of this phenomenon was given in 1905 by A. Einstein and independently in 1906 by the Polish physicist M. Smoluchowski (1872–1917). They developed the theory of the phenomenon, which made it possible to use the Brownian motion to confirm the molecular-kinetic theory.

Essentially, this phenomenon consists in the following. Suspended particles form, together with liquid molecules, a single statistical system. In accordance with the principle of equipartition of energy, the energy per degree of freedom of a Brownian particle is equal to $(1/2)kT$. The energy of $(3/2)kT$ corresponding to three translational degrees of freedom of a particle leads to the motion of its centre of mass, which is observed through the microscope as vibration. If a Brownian particle behaves like a rigid body, its vibrational degrees of freedom are responsible for another $(3/2)kT$ of energy. Therefore, the particle experiences constant changes in spatial orientation during its vibrational motion.



Albert
Einstein
(1879-1955)

It is easier to observe rotational Brownian motion not of the particles suspended in water but of some other objects. Hence, when we consider the Brownian movement of particles suspended in water, we mean the vibration of their centres of mass.

RANDOM WANDERING. As a result of random collisions between particles, their mean kinetic energies level out, while the motion of each of the colliding particles is a random process. Let us consider the position of a Brownian particle in certain fixed intervals of time. We place the origin of coordinates at the point O at which the particle was at the initial instant of time. Let us denote by q_i the vector characterizing the displacement of the particle between the $(i-1)$ st and i th observations. After n observations, the particle will move from the initial position to a point characterized by the radius vector r_n (Fig. 22):

$$r_n = \sum_{i=1}^n q_i. \quad (13.1)$$

In the intervals of time between observations, the particle moves not along a straight line but along a broken line as complex as the one describing the movement from the initial point to the point having the radius vector r_n . We can carry out a series of experiments with a Brownian particle starting from the origin and arriving after n steps at a certain point with a radius vector r_n . Clearly, all r_n 's will be different.

Let us calculate the mean square of the separation of a particle from the origin after n steps in a large series of experiments. Obviously,

$$\langle r_n^2 \rangle = \left\langle \sum_{i,j=1}^n q_i \cdot q_j \right\rangle = \sum_{i=1}^n \langle q_i^2 \rangle + \sum_{i \neq j} \langle q_i \cdot q_j \rangle, \quad (13.2)$$

where $\langle q_i^2 \rangle$ is the mean square of the displacement during the i th step in the series of experiments (naturally, it will be the same for all the steps and equal to a certain positive quantity a^2), and $\langle q_i \cdot q_j \rangle$ in the second sum on the right-hand side is the mean value of the scalar product of the displacements made during the i th and the j th steps. It is obvious that these displacements are quite independent of one another, and the scalar product has positive values as frequently as negative ones. For this reason, all the summands of the second sum $\langle q_i \cdot q_j \rangle = 0$ ($i \neq j$), and Eq. (13.2) becomes

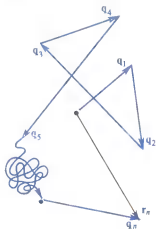


Fig. 22. Motion of a particle in the Brownian movement. Curved line depicts the motion from the 6th to $(n-1)$ st step

$$\langle r_n^2 \rangle = a^2 n = \frac{a^2}{\Delta t} t = \alpha t = \langle r_t^2 \rangle, \quad (13.3)$$

where Δt is the interval of time between observations and $t = \Delta t n$ is the time during which the mean square of separation of the particle became equal to $\langle r_t^2 \rangle$. Consequently, in spite of the fact that the directions along which the particle moves in each step are equally probable, the particle will on the average move away from the origin. This becomes especially clear if instead of many experiments with different Brownian particles we imagine a single experiment with many similar Brownian particles placed at the origin. Obviously, this "spot" of Brownian particles will spread from the origin, which just means that the root-mean-square deviation increases with time. It is essential that the mean square deviation in (13.3) grows in exact proportion to the first power of time.

CALCULATION OF THE MOTION OF A BROWNIAN PARTICLE. In order to characterize the Brownian movement, we must determine α in formula (13.3). On the one hand, it can be found experimentally by measuring $\langle r_t^2 \rangle$ or calculated theoretically on the other hand.

A Brownian particle moves under the action of $\mathfrak{m}$ random force appearing as a result of random collisions of molecules with the particle. We denote by b the friction coefficient for a particle in a liquid due to its viscosity. The equation of motion of the particle has the form

$$m\ddot{x} = -b\dot{x} + F_x, \quad (13.4)$$

where $\mathfrak{m}$ is the particle mass and F_x is the random force acting on it.

It should be noted that the term $-b\dot{x}$ is also due to bombardment of molecules. However, as the Brownian particle systematically moves at $\mathfrak{m}$ velocity $\dot{x}$, the momentum due to random impacts of molecules in the direction opposite to the motion of the particle is on the average larger than the momentum due to random impacts in the direction of motion. This leads to $\mathfrak{m}$ force of friction characterized by the quantity $-b\dot{x}$.

The equations of motion for quantities corresponding to other coordinate axes have a similar form.

Let us multiply both sides of this equation by x and transform the terms $\dot{x}\dot{x}$ and $\ddot{x}x$:

$$x\ddot{x} = (x^2/2)'' - (\dot{x})^2, \quad x\dot{x} = (x^2/2)'; \quad (13.5)$$

Equation (13.4) then assumes the form

$$(m/2)(\dot{x}^2)'' - m(\ddot{x})^2 = -(b/2)(\dot{x}^2)' + F_x x. \quad (13.6)$$

Let us average both sides of this equation over the Brownian particle ensemble considering that the average time derivative is equal to the derivative of the mean value, since the averaging is carried out over the ensemble of particles and is consequently transposable with the differentiation with respect to time. As a result of averaging Eq. (13.6), we obtain

$$(m/2)(\langle \dot{x}^2 \rangle)'' - \langle m(\ddot{x})^2 \rangle = -(b/2)(\langle \dot{x}^2 \rangle)' + \langle F_x x \rangle. \quad (13.7)$$

Since the deviation of a Brownian particle is equally probable in all directions, we obtain $\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle = \langle r^2 \rangle/3$. Hence Eq. (13.3) gives $\langle x^2 \rangle = \alpha t/3$, and consequently $(\langle x^2 \rangle)' = \alpha/3$ and $(\langle x^2 \rangle)'' = 0$. The random nature of the force F_x and the particle coordinate x , as well as their independence from each other imply that $\langle F_x x \rangle = 0$. Consequently, Eq. (13.7) can be reduced to the form

$$\langle m(\ddot{x})^2 \rangle = \alpha b/6. \quad (13.8)$$

According to the law of equipartition of energy among the degrees of freedom, we have $\langle m(\ddot{x})^2 \rangle = kT$. This gives the following expression for α from Eq. (13.8):

$$\alpha = 6kT/b, \quad (13.9)$$

where b which characterizes the force of liquid friction acting on a Brownian particle can be expressed theoretically (Stokes formula), measured experimentally, and assumed to be known. The temperature T is also known. Hence, formula (13.3) provides the following solution for the Brownian movement of suspended particles if we take into account Eq. (13.9):

$$\langle r^2 \rangle = 6kT/b. \quad (13.10)$$

If k is assumed to be measured in experiments on the verification of the Boltzmann distribution (see Sec. 9), all the quantities in this formula are known. We can experimentally verify this relation concerning the correctness of dependence on different parameters. The dependencies predicted by formula (13.10) were confirmed in experiments carried out from 1908 onwards by J. B. Perrin (1870–1942). Assuming now that this formula is valid, we can use it for refining and determining the value of the Boltzmann constant k , since all the remaining quantities in this formula can be measured independently. Such measurements of k were also carried out

by Perrin, and the results were in good agreement with the value of k obtained from the measurements concerning the Boltzmann distribution. The closeness of these results was a great triumph for the molecular-kinetic concepts at that time (the first quarter of the 20th century).

The following question arises in connection with (13.10). The quantity $\langle r^2 \rangle$ is independent of mass, since, as it can be directly seen from the Stokes formula, b depends only on the radius of the particle and not on its mass:

$$b = 6\pi\mu r_0, \quad (13.11)$$

where μ is the viscosity of the liquid, and r_0 is the radius of a spherical particle moving in the liquid.

On the other hand, the average velocity of the particle decreases with increasing mass for the same value of the mean energy. Hence the heavier particles vibrate less intensely than the lighter particles, other conditions being the same. It can be asked: how can light and heavy particles, which have entirely different intensities of vibrations, escape from the origin with identical average velocities? The answer is that the lighter particles really move more intensely than the heavier particles, but the ultimate result is that the mean velocity of escape from the origin is the same for all motions. In this respect, it can be stated that the motion of light particles can be characterized as "much movement and no results".

ROTATIONAL BROWNIAN MOVEMENT. A quantitative investigation of the rotational Brownian movement is difficult for particles suspended in a liquid. This can be done more easily with the help of a small light mirror suspended from an elastic string. The interaction with air molecules results in a statistical equilibrium, and each degree of freedom of the mirror must have an energy equal to $kT/2$. Consequently, the mirror will undergo torsional vibrations about an axis coinciding with the vertical string from which it is suspended. If the mirror surface is illuminated by a ray of light, the reflected ray is strongly deviated even for quite small rotations of the mirror. Consequently, even small torsional vibrations can be observed and measured.

Let us calculate the mean square angular amplitude of these vibrations. Let D be the torsion modulus of the thread, and J the moment of inertia of the mirror with respect to the torsion axis. The angle of rotation of the mirror with respect to the equilibrium position is denoted by φ . The equation for torsional vibrations has the form

$$J\ddot{\varphi} = -D\varphi, \quad (13.12)$$

?

The average velocity of a Brownian particle depends on its mass, while the mean square deviation of the particle from the origin over a fixed interval of time is independent of its mass. Why are light particles involved in "much movement and no results" unlike heavier particles that move slowly?

Explain why average force acting on a particle at rest due to impacts of molecules is equal to zero, while the force acting on a moving particle is not equal to zero. Prove that this force is proportional to the first power of the particle velocity and is directed against the motion.

where the minus sign indicates that the moment of elastic forces of the string tends to return the mirror to its equilibrium position. Multiplying both sides of the above equation by $\dot{\phi}$ and integrating, we obtain the law of conservation of energy for vibrations of the string:

$$(1/2)J\dot{\phi}^2 + (1/2)D\phi^2 = \text{const.} \quad (13.13)$$

Since the small torsional vibrations are harmonic, we get

$$(1/2)J\langle\dot{\phi}^2\rangle = (1/2)D\langle\phi^2\rangle = (1/2)kT, \quad (13.14)$$

where we have used the law of equipartition of energy. This gives the following expression for the Brownian torsional vibrations of the mirror:

$$\langle\phi^2\rangle = kT/D. \quad (13.15)$$

This quantity can be measured. For example, at $T \simeq 290$ K, and $D \simeq 10^{-15}$ N·m, we get $\langle\phi^2\rangle \simeq 4 \times 10^{-6}$, which can be measured experimentally. Knowing the parameters of the string and the temperature, and measuring $\langle\phi^2\rangle$, we can find the value of the constant k with the help of formula (13.14). The values of k obtained in this way are in good agreement with those given by the Boltzmann distribution and the translational Brownian movement.

Thus, the Brownian movement offers a direct method of determining the molecular constant k by measuring the macroscopic parameters. On the other hand, an analysis of gases which can be described quite well by the ideal gas equation $pV = \nu RT$ gives the molar gas constant which is also a macroscopic quantity. Knowing R and k , we can use formula (10.7) to determine another important quantity characterizing the microscopic properties of systems, viz. the Avogadro number (see (10.6)):

$$N_A = R/k. \quad (13.16)$$

Example 13.1. Find the maximum sensitivity of a mirror galvanometer with internal resistance $R = 200$ k Ω . The maximum deviation of the mirror in an aperiodic regime is attained after the passage of time $\tau = 20$ s. The fraction of energy q stored as the potential energy of the wound spring is equal to 0.3 of the supplied energy. The temperature is equal to 27°C. The minimum current that can be reliably detected by the galvanometer is assumed to cause deviations which must exceed the thermal vibrations of the pointer by $n = 3$ times.

The energy supplied to the galvanometer from the external

circuit during the establishment of the steady state is

$$W = \tau R I^2. \quad (13.17)$$

A part of this energy (q) is stored as the potential energy of the galvanometer spring:

$$U = qW = q\tau R I^2. \quad (13.18)$$

According to the equipartition law, the mean thermal vibration energy of the galvanometer is equal to $\langle W_{\text{therm}} \rangle = kT/2$. In accordance with (13.18), such vibrations are equivalent to current spikes

$$\langle (\Delta I)^2 \rangle = \langle W_{\text{therm}} \rangle / q\tau R = kT / (2q\tau R). \quad (13.19)$$

The minimum current $I_{\min}$ must be n times larger than $(\langle \Delta I^2 \rangle)^{1/2}$. Hence

$$I_{\min} = n(\langle \Delta I^2 \rangle)^{1/2} = n[kT / (2q\tau R)]^{1/2} = 1.25 \cdot 10^{-13} \text{ A}.$$

PROBLEMS

- 1.1. From a pack of n cards, take $m < n$ cards set beforehand. Find the probability that m cards taken at random from the pack will all be set beforehand?
- 1.2. An urn contains n white and m black balls. Find the probability that a white ball will be taken out in three successive trials (a) if the previously extracted ball is returned into the urn and (b) if it is not returned.
- 1.3. An urn contains n different balls. We fix a sequence of m specific balls. Find the probability of extracting these balls in the sequence if they are extracted at random and are not returned.
- 1.4. Find the relative number of nitrogen molecules at 27°C , whose velocities lie in the interval from 260 to 270 m/s.
- 1.5. Find the mean absolute velocity and the variance of velocity of hydrogen molecules at 27°C .
- 1.6. At what height will the partial pressure of nitrogen decrease to $3/2$ of its initial value? Assume that the temperature of atmosphere is constant and equal to 0°C .
- 1.7. Find the mean fluctuational deviation of a pendulum whose mass is 30 mg and length 3 cm at 27°C .
- 1.8. Find the sensitivity limit for a galvanometer with internal resistance $R = 50 \text{ k}\Omega$. The maximum deviation in an aperiodic regime is attained in $\tau = 10 \text{ s}$. When deflection is established, 80% of energy is converted into Joule's heat. The temperature is 27°C . For a reliable detection of the current it is necessary that it cause 3 times larger deflection than thermal fluctuations.
- 1.9. Find the frequency of collisions of H_2 molecules with the surface area of 1 cm^2 at a pressure $p = 9.8 \times 10^4 \text{ Pa}$ and $t = 300^\circ\text{C}$.
- 1.10. A balloon with 1 m diameter contains 4 kg of helium at 300 K. Find the frequency of collisions of a molecule with the wall.

- 1.11. The moment of inertia of an oxygen molecule with respect to the rotational axis is $J = 1.9 \times 10^{-46} \text{ kg} \cdot \text{m}^2$. Find the mean cyclic frequency of rotation at 50°C .
- 1.12. An ideal gas is under standard conditions. Find volume V in which the mean square fluctuation of the number of particles amounts to 10^{-8} of the average number of particles in this volume.
- 1.13. Calculate the fluctuation of the kinetic energy of translatory motion of an ideal gas molecule at a temperature T .
- 1.14. Find the mean square velocity of a hydrogen molecule at $T = 10^6 \text{ K}$.
- 1.15. Find the total mean kinetic energy of motion of diatomic gas molecules contained in a 4 l vessel under the pressure $1.47 \times 10^5 \text{ Pa}$.
- 1.16. A typist has typed 1000 pages of a text and made 140 mistakes. What is the probability that a page taken at random contains no mistakes? Has one mistake? Two mistakes? Error distribution is described by the Poisson law.
- 1.17. Estimate the order of magnitude of the total number of molecules in the Earth atmosphere considering that the density of molecules is described by the barometric formula at $T = 273 \text{ K}$ (the Earth radius is 6370 km).
- 1.18. Find the mean value of the x-component of the velocity of gas molecules moving in the positive direction of the X-axis. The temperature is T and the mass of the molecules m .
- 1.19. Using the Poisson distribution (5.23), find the mean square fluctuations of the number of particles in a certain small volume of the gas.
- 1.20. Natural carbon is a mixture of ^{12}C and ^{13}C isotopes (we neglect the ^{14}C isotope). The atomic mass of natural carbon is $A = 12.01115$. Find the number of moles of ^{12}C and ^{13}C isotopes contained in a mole of natural carbon.

ANSWERS

- 1.1. $\mathcal{P} = m!(n-m)!/(n!)$. 1.2. $\mathcal{P} = [n/(n+m)]^n$; $\mathcal{P} = n(n-1)(n-2)/[(n+m)(n+m-1)(n+m-2)]$. 1.3. $\mathcal{P} = (n-m)!/(n!)$. 1.4. $dn/n = 0.017$. 1.5. $\langle |v| \rangle = 1775 \text{ m/s}$; $\sigma = 749 \text{ m/s}$. 1.6. 3346 m. 1.7. $\sqrt{\langle \varphi^2 \rangle} = 2.2 \times 10^{-8}$. 1.8. $I_{\min} = 4.3 \times 10^{-13} \text{ A}$. 1.9. $v = 1.1 \times 10^{22} \text{ s}^{-1}$. 1.10. 1320 s^{-1} . 1.11. $\sqrt{\langle \omega^2 \rangle} = 4.7 \times 10^{12} \text{ s}^{-1}$. 1.12. $V = 3.7 \times 10^{-10} \text{ m}^3$. 1.13. $\sqrt{\langle [\Delta(mv^2/2)]^2 \rangle} = \sqrt{3/2} kT$. 1.14. $\approx 5 \times 10^5 \text{ m/s}$. 1.15. $\approx 1500 \text{ J}$. 1.16. 0.79; 0.19; 0.02. 1.17. $\approx 10^{44}$. 1.18. $[kT/(2\pi m)]^{1/2}$. 1.19. $\langle (\Delta m)^2 \rangle = \langle m \rangle$. 1.20. $v_1 = 0.98885$; $v_2 = 0.01115$.



Thermodynamic Method

Main idea: a many-particle system must obey certain general laws like the law of conservation of energy. These laws are called the laws of thermodynamics. The macroscopic state of a system is characterized by parameters which have quite definite values. The behaviour of the system is described phenomenologically on the basis of the laws of thermodynamics.

Mathematical apparatus: the theory of differential forms and partial differential equations.

Sec. 14. THE FIRST LAW OF THERMODYNAMICS

The objectives of thermodynamics are discussed and the definitions of work, amount of heat, and internal energy of the system are given. The first law of thermodynamics is formulated.

THE OBJECTIVES OF THERMODYNAMICS. Thermodynamics aims at studying phenomenologically the properties of material bodies, characterized by macroscopic parameters, on the basis of general laws called the laws of thermodynamics without resorting to the microscopic mechanisms of phenomena under investigation (see Sec. 1). Thermodynamics is based on three laws. The first law is the law of conservation of energy, applied to thermodynamics phenomena. The second law determines the direction of the evolution of thermodynamic processes. The third law imposes constraints on the processes, thus excluding processes which lead to zero thermodynamic temperature.

As in the previous chapter dealing with statistical method, the ideal gas model will be used here for illustrating the thermodynamic method. However, the method studied with the help of this simplest model is itself applicable to other models of specific substances, just as in the case of the statistical method.

WORK. In order to reduce the volume occupied by a gas, a certain amount of work must be done to overcome the forces of pressure in the gas. Suppose that a gas is contained in a cylindrical vessel with a piston by moving which we can change the volume of the gas (Fig. 23). The force acting on the piston with area S due to pressure p is equal to pS , and

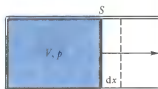


Fig. 23. To the derivation of the expression for work

hence the work done in displacing the piston by dx is $pS dx = p dV$, where dV is the change in the gas volume. It is assumed that the work done on the gas by external forces is negative, while the work performed by the expanding gas is positive. Hence, the work δA done by the gas in changing its volume by dV is

$$\delta A = p dV. \quad (14.1)$$

This and subsequent formulas were derived in the assumption of equilibrium process (see Sec. 16)

The rationale for the notation δA rather than dA for work will be given later.

If we consider a more complex system instead of an ideal gas, other ways of performing work on the system or by the system are also possible. The typical feature of these processes is that by changing certain macroscopic parameters, energy is supplied or taken away from the system. This statement is very important, since energy can be supplied to or taken away from a system without changing its macroscopic parameters. We cannot say that work is done in this case. By way of an example, we can consider the transfer of energy to a system by supplying heat. In this case it cannot be said that work is done on the system. Macroscopic parameters of the system are changed as a result of heat transfer.

In the general case, the expression for work has the following form. We denote the parameters whose change is associated with accomplishing work by $\zeta_1, \zeta_2, \dots$. For an infinitely small change in the parameter ζ_i by $d\zeta_i$, the work $\delta A = f_i d\zeta_i$ is done, where f_i is the generalized force. The signs are chosen in the same way as in (14.1): if the work is done on the system, the δA must have the negative sign. The total work involving a change in all the parameters is

$$\delta A = f_1 d\zeta_1 + f_2 d\zeta_2 + \dots \quad (14.2)$$

The term given by (14.1) can be considered to be included among the terms $f_i d\zeta_i$. For example, the generalized force $f_1 = p$ and the generalized coordinate $\zeta_1 = V$, i.e. $d\zeta_1 = dV$. However, for simplifying the notation and retaining the visual form, we shall usually write only the term (14.1) omitting all the other terms in (14.2), which are possible in principle. We shall write additional generalized forces and corresponding coordinates explicitly only when it is required for a specific problem. However, it is expedient to consider some examples.

Under the action of force f , a rod is either stretched or



Julius Robert
von Mayer
(1814-1878)

compressed. The work done upon a change in its length by dl is

$$\delta A = -f dl,$$

where f is the magnitude of the force. The minus sign indicates that in order to elongate the rod, the work must be done on the system. Consequently, in accordance with the sign rule adopted in (14.2), the work is negative.

The work done in the transfer of electric charge dq between two points with the potential difference φ is equal to $\delta A = -\varphi dq$,

where φ is the absolute value of the potential difference. The charge dq is transferred in the direction of increasing potential. This example illustrates the fact that generalized forces and coordinates in (14.2) do not necessarily resemble ordinary forces and coordinates.

HEAT. It is known from experiments that when two bodies are brought into contact, their thermal states equalize. It is said that heat is transferred from the warmer body to the colder one. Heat is a special form of energy, viz. the form of molecular motion. We shall denote by δQ an infinitely small amount of this energy having the indicated specific form. In this form, i.e. in the form of heat, the energy can be either supplied to a system or removed from it. It was assumed that δQ is positive if heat is supplied to a system and negative if heat is removed from it.

The concept of work appeared in engineering in the middle of the 18th century as a measure of efficiency of water-lifting machines. Later, this concept was used in mechanics. L. Carnot (1753-1823) was the first to define this quantity as the product of the force, distance, and the cosine of the angle between them. In the first half of the 19th century this term was used more and more widely in applied mechanics. On the other hand, it is employed in the analysis of the processes of mutual conversion of heat and work, which was started by S. Carnot in 1824.

INTERNAL ENERGY. This is the energy associated with all possible movements of particles constituting a system and their interactions, including the energy due to the interaction and motion of particles constituting complex particles. It follows from this definition that the internal energy does not include the kinetic energy of the motion of the centre of mass of the system, i.e. the motion of the system as a whole, and the potential energy of the system in external fields. All other types of kinetic and potential energies of the particles in the system, including the energies of particles constituting complex particles, pertain to internal energy.

! The first law of dynamics does not determine the nature of a process. However, any process occurring in a thermodynamic system must obey this law. This allows us to study the peculiarities of various processes with the help of this law.



Hermann Ludwig
Ferdinand
von Helmholtz
(1821-1894)

An infinitely small change in internal energy is denoted by dU . It is assumed that dU is positive if the internal energy of the system increases and negative if it decreases.

The parameters can be divided into intrinsic and extrinsic. Extrinsic parameters characterize external conditions of the system, while intrinsic parameters are those which are established in the system after we fix external conditions. Depending on circumstances, the same parameter may be extrinsic or intrinsic. For example, we can fix the volume V of a gas. This is an extrinsic parameter. At a given temperature, a definite pressure p will be established in the system, which is an intrinsic parameter.

Let us imagine another situation. A volume is bounded by a sliding piston moving vertically. A certain load is placed on the piston. In this case the pressure p of the gas is determined by external conditions, while the volume at a given temperature will be established in accordance with this pressure. Thus, here volume is an intrinsic parameter, while pressure is an extrinsic parameter.

THE FIRST LAW OF THERMODYNAMICS. The law of conservation of energy for heat as a form of energy, internal energy and the work done, taking into account the sign rule for these quantities, can be written in the following obvious form:

$$\delta Q = dU + \delta A. \quad (14.3)$$

The law of conservation of energy in the form (14.3) is called the **first law of thermodynamics**. It differs in principle from the law of conservation of energy in mechanics in the quantity δQ called an infinitely small amount of heat. Thermodynamics studies the motion and transformation of this form of energy.

Below, we shall mainly consider the work connected with forces of pressure and changes in volume. Hence, we shall use the following form of the first law of thermodynamics:

$$\delta Q = dU + p dV, \quad (14.4)$$

?

The internal energy, as well as heat, is determined by the energy conditions on molecular level. What is the difference between them?

since the term $p dV$ is always present on the right-hand side of (14.3), while other terms that are possible in principle are absent. However, when necessary, the right-hand side of formula (14.4) can always be supplemented with the terms of the form (14.2).

Just as in mechanics, the law (14.3) of conservation of

energy cannot predict the direction of evolution of a process. It can only be used to indicate how the quantities change during a process. In mechanics, the motion is described by equations of motion. The direction of evolution of processes in thermodynamics is described by the second law of thermodynamics (see Secs. 20, 22).

The establishment of the first law of thermodynamics is connected with the discovery of the law of conservation and transformation of energy, which emerged as a result of the evolution of physics by the middle of the 19th century. The merit of establishing the conservation law belongs to R. Mayer, J. Joule, and H. Helmholtz. The first work by Mayer in this field was published in 1840. The works by Joule and Helmholtz where this law was formulated appeared in 1847. They had to overcome considerable difficulties before the validity of this law was recognized.

Example 14.1. Calculate the internal energy of 1 l of helium under a pressure $p = 9.8 \times 10^4$ Pa and $t = 0^\circ\text{C}$.

According to the law of equipartition of energy, the mean energy per helium atom is $\langle \epsilon \rangle = (3/2)kT$. In the volume V of a gas, there are $n = Vp/(kT)$ particles. Consequently, the internal energy of 1 l of helium is

$$U = \frac{3}{2}kT \frac{Vp}{kT} = \frac{3Vp}{2} = 147 \text{ J.}$$

Example 14.2. Analyze the process of transformation of energy when work is done on a gas.

Suppose that ν moles of a gas are contained in a vertical cylinder under the piston of area S and mass m_0 compressed by the weight of the piston and the external atmospheric pressure p_{at} . Thus, the initial pressure under the piston is $p_{at} + m_0g/S$. Suppose that the piston consists of a thin plate loaded by sand. We can remove a grain of sand of mass dm . As a result, the piston goes up by a distance dx . This rise occurs so slowly that the temperature of the gas under the piston is equal to a constant temperature T_0 of the atmospheric air, and the gas pressure under the piston becomes $p_{at} + (m_0 - dm)g/S$. In this case, the volume of the gas under the piston increases by $dV = Sdx$. The work performed by the gas is $(p - p_{at})Sdx = (p - p_{at})dV$. The work done for increasing volume from V_0 to V is equal to

$$A = \int_{V_0}^V (p - p_{at})dV. \quad (14.5)$$

Since the process occurs infinitely slowly, we can assume that the gas under the piston is in an equilibrium state, and



The first law of thermodynamics is an expression of the law of conservation of energy for processes involving heat. The work is associated with the energy transfer by changing macroscopic parameters, while heat transfer is accomplished through the transfer of energy of molecular motion. The change of macroscopic parameters occurring in this case is the result of the change in energy conditions on molecular level.



James Prescott
Joule
(1818-1889)

the following relation holds between its pressure and volume: $p = \nu RT_0/V$. Substituting this expression into (14.5) for p and integrating, we obtain the work performed by the gas to increase its volume from V_0 to V :

$$A = \nu RT_0 \ln(V/V_0) - p_{at}(V - V_0). \quad (14.6)$$

In this case, the piston is lifted by $\Delta x = (V - V_0)/S$, and the gas energy is converted into the potential energy of the piston and the grains of sand. To verify this, let us calculate the work done to lift the piston with sand. The force of gravity against which this work is done is $F = m(x)g$, where $m(x)$ is the mass of the piston with sand at a height x . Measuring the coordinate x from the bottom of the cylinder, we obtain $m(x_0) = m_0$, $x_0 S = V_0$, and $xS = V$.

The work done in lifting a varying mass is

$$A = \int_{x_0}^x m(x)g dx.$$

For determining $m(x)$, we use the inequality

$$m(x)g = S(p - p_{at}) = S\nu RT_0/V - Sp_{at} = \nu RT_0/x - Sp_{at},$$

whence

$$A \int_{x_0}^x m(x)g dx = \nu RT_0 \ln(x/x_0) - Sp_{at}(x - x_0), \quad (14.7)$$

which coincides with (14.6). The gas in the cylinder is the source of energy for accomplishing this work. It will be seen later, however, that the internal energy of an ideal gas does not change in this case, and the entire energy converted into the potential energy is supplied in the form of heat to the gas by the surrounding medium.

Considering (14.7), Eq. (14.5) can be written in the form

$$\int_{V_0}^V p dV = \int_{V_0}^V p_{at} dV + \int_{x_0}^x m(x)g dx. \quad (14.8)$$

This means that the work accomplished by the gas during its expansion in the cylinder is spent to overcome the atmospheric pressure on the piston and to surmount the weight of the piston (with sand). The weight of the gas in the cylinder is ignored.

Using (14.5), relation (14.8) can be written in a different form. It will be shown later that the internal energy U of an ideal gas depends only on temperature. The process under

consideration occurs at a constant temperature, and hence $dU = 0$ for this process. Substituting $p dV = \delta Q$ from (14.5) into (14.8), we get

$$\int_{T=\text{const}} \delta Q = \int_{V_0}^V p_{\text{at}} dV + \int_{x_0}^x m(x) g dx. \quad (14.9)$$

In this expression, δQ denotes the amount of heat supplied to the gas under the piston by the surrounding medium at a constant temperature (thermostat). Thus, the work performed by an ideal gas in expansion at a constant temperature is done at the expense of the energy supplied to the gas in the form of heat by the surrounding medium (thermostat). If the cylinder walls are heatproof (adiabatic), heat cannot be transferred from the surrounding medium. In this case, the work on expansion of the gas is done at the expense of its internal energy: the internal energy decreases, and the gas temperature becomes lower. Under these conditions, we have the following expression for the law of conservation of energy instead of (14.9):

$$-\int_{\delta Q=0} dU = \int_{V_0}^V p_{\text{at}} dV + \int_{x_0}^x m(x) g dx. \quad (14.10)$$

Here, however, the dependence of m on x is quite different from that in (14.9). This dependence is determined by the law of adiabatic expansion of a gas (see Sec. 18).

Sec. 15. DIFFERENTIAL FORMS AND TOTAL DIFFERENTIALS

The conditions under which a differential form is a total differential are analyzed. The connection between the total differential and the existence of a function of state is discussed.

DIFFERENTIAL FORMS. Infinitesimal quantities δQ , dU , and δA in (14.3) are denoted differently: some by using the symbol d and the others with the help of the symbol δ . The reason behind the use of different notations is the difference in the properties of these infinitesimals.

Suppose that we have certain independent variables. At first we consider one independent variable, for example, x . The differential of this quantity is dx . Let $f(x) dx$ be an infinitely small quantity, where $f(x)$ is an arbitrary function. It can be asked whether this infinitesimal quantity can be represented as an infinitesimal increment of a certain function $F(x)$ at two neighbouring points separated by dx , i.e. in the form

$$f(x) dx = F(x + dx) - F(x). \quad (15.1)$$

In most cases it is possible. Here, however, we shall not stop to consider certain mathematical details connected with nondifferentiable functions, and so on. It would be sufficient to state that it can be done if for $F(x)$ we take the primitive of $f(x)$, i.e.

$$F(x) = \int f(x) dx. \quad (15.2)$$

Hence, in the case of one variable, it is almost always possible to consider an infinitesimal as an infinitely small increment of a certain function. In this case, the infinitely small quantity $f(x)dx$ is called the total differential. As an infinitely small increment of the function F , it can be written in the form

$$dF(x) = f(x) dx. \quad (15.3)$$

Here the symbol d denotes an infinitely small increment of the function.

For most cases of two and more variables, the situation is different. Suppose that for two variables there exists an infinitely small quantity

$$\sigma = \mathcal{P}(x, y)dx + Q(x, y)dy, \quad (15.4)$$

where $\mathcal{P}(x, y)$ and $Q(x, y)$ are certain functions of x and y . Here we did not use symbols d or δ to denote an infinitesimal, since it is not yet clear which of the symbols must be used. We must find out whether this quantity can be represented as an increment of a certain function $F(x, y)$ of the variables x and y at two neighbouring points, i.e. in the form $F(x + dx, y + dy) - F(x, y) = \sigma$ provided that such a representation must be possible for independent variations of the arguments. It turns out that in the general case of arbitrary $\mathcal{P}$ and Q this is impossible.

TOTAL DIFFERENTIAL. The representation is possible only if a certain relation exists between $\mathcal{P}$ and Q . Let us write the required condition:

$$\mathcal{P}(x, y)dx + Q(x, y)dy = F(x + dx, y + dy) - F(x, y). \quad (15.5)$$

We expand $F(x + dx, y + dy)$ into a series in dx and dy and confine ourselves to the first term:

$$F(x + dx, y + dy) = F(x, y) + \frac{\partial F}{\partial x} dx + \frac{\partial F}{\partial y} dy. \quad (15.6)$$

Then Eq. (15.5) becomes

$$\mathcal{P} dx + Q dy = \frac{\partial F}{\partial x} dx + \frac{\partial F}{\partial y} dy. \quad (15.7)$$

Since x and y are independent quantities, it follows from this equation that

$$\mathcal{P} = \frac{\partial F}{\partial x}, \quad Q = \frac{\partial F}{\partial y}. \quad (15.8)$$

Differentiating $\mathcal{P}$ with respect to y and Q with respect to x , we obtain

$$\frac{\partial \mathcal{P}}{\partial y} = \frac{\partial^2 F}{\partial y \partial x}, \quad \frac{\partial Q}{\partial x} = \frac{\partial^2 F}{\partial x \partial y}. \quad (15.9)$$

Mixed derivatives are independent of the order of differentiation: $\partial^2 F / (\partial x \partial y) = \partial^2 F / (\partial y \partial x)$, and hence

$$\frac{\partial \mathcal{P}}{\partial y} = \frac{\partial Q}{\partial x}. \quad (15.10)$$

Thus we have proved that an infinitely small quantity (15.4) can be represented as an infinitesimal increment of another function $F(x, y)$ in the form (15.5) or (15.7), if the functions $\mathcal{P}$ and Q satisfy condition (15.10) which is the necessary and sufficient condition. In this case, an infinitely small quantity (15.4) is called the **total differential** and is denoted with the help of (15.7) as

$$\sigma = \mathcal{P} dx + Q dy = \frac{\partial F}{\partial x} dx + \frac{\partial F}{\partial y} dy = dF. \quad (15.11)$$

This symbol indicates in an explicit form the quantity F whose increment is considered.

On the other hand, if condition (15.10) did not hold, σ would be an infinitesimal that cannot be represented as an increment of the other function. This quantity could be denoted, for example, by the symbol δL . In this case, however, L does not denote a quantity which can be ascribed a definite meaning under given conditions. Letter L in this type of expressions denotes the property of a physical quantity under consideration which distinguishes it from other quantities, symbol δ indicating that we are dealing with an infinitely small amount of this quantity. Hence symbol δL is a single entity having a quantitative significance only for infinitely small value.

The basic property of infinitesimals that are total

differentials is that the value of the integral

$$\int_{(x_1, y_1)}^{(x_2, y_2)} (\mathcal{P} dx + Q dy) \quad (15.12)$$

over these quantities between two arbitrary points (x_1, y_1) and (x_2, y_2) depends on the positions of the initial and final points but is independent of the integration path. It should be noted that if condition (15.11) is satisfied, the integral (15.12) is evaluated by the formula

$$\int_{(x_1, y_1)}^{(x_2, y_2)} (\mathcal{P} dx + Q dy) = \int_{(x_1, y_1)}^{(x_2, y_2)} dF = F(x_2, y_2) - F(x_1, y_1). \quad (15.13)$$

This formula shows explicitly that the integral over an infinitely small quantity that is the total differential is indeed independent of the integration path and depends only on the initial and final points.

If the variables x and y characterize a state of some system and if infinitesimal of the form (15.4) is the total differential of the function F , the function F is said to be a function of state, i.e. the function which has a quite definite value in a given state of the system, and this value does not depend on the way or method by which the system is transferred to this state.

The functions of state are its most important characteristics.

Let us consider two differential forms:

$$\sigma_1 = x dy + y dx, \quad (15.14)$$

$$\sigma_2 = x dy - y dx \quad (15.15)$$

and evaluate the integrals between the points (x_0, y_0) and (x_1, y_1) along two different paths parallel to coordinate axes (Fig. 24). We denote the path $(x_0, y_0) \rightarrow (x_0, y_1) \rightarrow (x_1, y_1)$ by L_1 and $(x_0, y_0) \rightarrow (x_1, y_0) \rightarrow (x_1, y_1)$ by L_2 . Then

$$\begin{aligned} I_1(\sigma_1) &= \int_{L_1} (x dy + y dx) = \int_{(x_0, y_0)}^{(x_0, y_1)} (x dy + y dx) \\ &+ \int_{(x_0, y_1)}^{(x_1, y_1)} (x dy + y dx) \\ &= x_0(y_1 - y_0) + y_1(x_1 - x_0) = y_1x_1 - x_0y_0, \end{aligned} \quad (15.16)$$

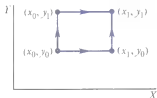


Fig. 24. Different integration paths for the transition from point (x_0, y_0) to (x_1, y_1)

$$\begin{aligned}
 I_2(\sigma_1) &= \int_{L_2} (x \, dy + y \, dx) \\
 &= \int_{(x_0, y_0)}^{(x_1, y_0)} (x \, dy + y \, dx) + \int_{(x_1, y_0)}^{(x_1, y_1)} (x \, dy + y \, dx) \\
 &= y_0(x_1 - x_0) + x_1(y_1 - y_0) = y_1x_1 - x_0y_0. \quad (15.17)
 \end{aligned}$$

Obviously, $I_1(\sigma_1) = I_2(\sigma_2)$. For the form σ_2 we have

$$\begin{aligned}
 I_1(\sigma_2) &= \int_{L_1} (x \, dy - y \, dx) = x_0(y_1 - y_0) - y_1(x_1 - x_0) \\
 &= 2x_0y_1 - x_0y_0 - y_1x_1, \quad (15.18)
 \end{aligned}$$

$$\begin{aligned}
 I_2(\sigma_2) &= \int_{L_2} (x \, dy - y \, dx) = y_0(x_1 - x_0) - x_1(y_1 - y_0) \\
 &= 2x_1y_0 - x_0y_0 - x_1y_1. \quad (15.19)
 \end{aligned}$$

Naturally, $I_1(\sigma_2) \neq I_2(\sigma_2)$. Hence we can conclude that σ_2 is not a total differential, i.e. there is no function $F(x, y)$ for which $dF(x, y) = x \, dy - y \, dx$. We can also verify this with the help of (15.10). In the case under consideration, $\mathcal{P} = -y$, $Q = x$, $\partial\mathcal{P}/\partial y = -1$, and $\partial Q/\partial x = 1$, and hence $\frac{\partial\mathcal{P}}{\partial y} \neq \frac{\partial Q}{\partial x}$.

In the case of σ_1 the matter is not as simple. We can conclude on the basis of equality $I_1(\sigma_1) = I_2(\sigma_1)$ that σ_1 is the total differential only if we prove that this equality is valid for any paths connecting the initial and final points. We have checked this only for two paths. Thus, in order to be able to conclude definitely that σ_1 is the total differential we must either prove the equality $I_1(\sigma_1) = I_2(\sigma_1)$ for an arbitrary path, or use the criterion (15.10). The latter way is easier.

We have $\mathcal{P} = y$ and $Q = x$, and $\partial\mathcal{P}/\partial y = \partial Q/\partial x$ indeed. It can be easily seen that in this case $F(x, y) = xy + a$, where a is an arbitrary constant. This gives

$$dF(x, y) = d(xy + a) = x \, dy + y \, dx. \quad (15.20)$$

The integral between points (x_0, y_0) and (x_1, y_1) along L is calculated as follows:

$$\begin{aligned}
 \int_{(x_0, y_0)}^{(x_1, y_1)} (x \, dy + y \, dx) &= \int_{(x_0, y_0)}^{(x_1, y_1)} d(xy + a) \\
 &= [xy + a]_{x_0, y_0}^{x_1, y_1} = x_1y_1 - x_0y_0. \quad (15.21)
 \end{aligned}$$

Sec. 16. REVERSIBLE AND IRREVERSIBLE PROCESSES

The characteristics of processes and their classification are considered. The relationship between equilibrium and nonequilibrium, and reversible and irreversible processes is analyzed. It is noted that the concepts of infinitely slow and reversible processes are not equivalent.

PROCESSES. An equilibrium state is characterized by the values of macroscopic parameters p , V , and T . The macroscopic values and methods of measuring p and V do not require additional explanations. As regards temperature, we refer the reader to Sec. 11. However, we have not clarified within the framework of thermodynamic treatment what we mean by an ideal gas.

An ideal gas can be defined as the gas obeying the Boyle law in the following formulation: for a fixed mass of the gas, the product of pressure by the volume depends only on temperature. We have already established what is a constant "degree of heating", i.e. constant temperature. Therefore it is quite clear what we mean by verifying the validity of Boyle's law $pV = \text{const}$ for all possible temperatures, although the temperature itself is not yet determined. Consequently, we can check whether or not a gas is ideal even before we define how to measure temperature. If it is established that the gas is ideal we can postulate the temperature dependence of pV in the form (10.5). After this, the ideal gas is used as a thermometric body, while temperature is determined in accordance with (10.5) by taking, for example, p as the thermometric quantity. It is just the quantity defined in this way that will be called temperature and denoted below as T .

It is already almost clear that it is the same temperature T which was used in Chap. 1. A detailed justification of this concept will be given later. Thus it can be assumed that the third macroscopic parameter T characterizing an equilibrium state of the system is also defined.

We shall call a process the transition from one equilibrium state to another, i.e. from some values p_1 , V_1 , T_1 of the parameters to others, p_2 , V_2 , T_2 . In this definition, it is essential that the initial and final states are equilibrium states.

NONEQUILIBRIUM PROCESSES. Suppose, for example, that we must go over to a state with a different volume. Clearly, if we do it not very slowly, the pressure, as well as temperature, will no longer be constant over the volume. It would be in general meaningless to speak about any definite pressure or temperature, since they will be different at different points. Moreover, the distribution of pressure and temperature over the volume depends not only on the initial and final states but also on the way in which this transition is realized. Thus, intermediate states in such a process are nonequilibrium ones. This process is called nonequilibrium process.

! All intermediate states in an equilibrium process are equilibrium states, while the intermediate states of a nonequilibrium process include nonequilibrium states.

Equilibrium processes are reversible, while nonequilibrium processes are irreversible.

An infinitely slow process is not necessarily an equilibrium process and a reversible process.



The change of state of
 ■ system is always associated with a transition to
 ■ nonequilibrium state. The departure from the nonequilibrium state is the more significant, the faster the change in the system. A return to the equilibrium state requires a certain amount of time. Hence, by changing the state of
 ■ system quite slowly, we shall not take the system away from the equilibrium state on the one hand, and on the other hand, provide sufficient time for the system to return to the equilibrium state at each intermediate stage. Consequently, the system passes through
 ■ sequence of equilibrium states. It would be wrong to consider this statement to be approximate, and to assume that the system passes through a sequence of only nearly equilibrium, and not exactly equilibrium, states. As
 ■ matter of fact, the equilibrium state itself is attained through fluctuations via nonequilibrium states. Hence, if "nearly equilibrium states" differ from the equilibrium state by an amount smaller than the fluctuation states, they can be simply considered as equilibrium states. This can be always attained if the process is sufficiently slow.

EQUILIBRIUM PROCESSES. A transition can be accomplished in a different way, i.e. infinitely slowly. After an infinitely small change in parameters the next change is not made until the system attains an equilibrium state, i.e. all macroscopic parameters assume constant values over the entire system. After this the next step is made, and so on. Thus, the entire process consists of a sequence of equilibrium states. Such a process is called **equilibrium process**. It can be depicted on the diagrams by continuous curves. In the equation of state for an ideal gas, $pV_m = RT$, any two parameters can be considered as independent parameters characterizing the process. An example of the process of transition from the state p_1, V_1 to the state p_2, V_2 is shown in Fig. 25. At each point of the process, the temperature is uniquely determined by the equation of state.

REVERSIBLE AND IRREVERSIBLE PROCESSES. A process for which a reverse transition from the final state to the initial state occurs via the same intermediate states as for the forward process is called **reversible**.

A process is **irreversible** if the reverse process via the same intermediate state is impossible.

Obviously, a nonequilibrium process in principle cannot be reversible. On the other hand, an equilibrium process is always reversible.

It does not mean, however, that the concept of reversible process is equivalent to that of an infinitely slow process. Some infinitely slow processes are irreversible. For example, the plastic deformation of solids may occur infinitely slowly, but is nevertheless an irreversible process.

Unless otherwise stated, we shall be henceforth considering reversible processes only.

Let us return to Example 14.2 of isothermic expansion of a gas. After the gas has been expanded from V_0 to V , further removal of sand grains from the piston is discontinued. The gas has passed through a sequence of stages, in each of which it had definite values of pressure and volume, while the temperature was constant. As a result of the work done by the gas, the atmospheric air was pushed out of the volume which is now occupied by the gas in the cylinder, and the piston with sand was raised to a certain height. The grains of sand which are removed in order to raise the piston are located at different heights. Let us now gradually reload the piston with sand grains, which were removed earlier in order to raise the piston, and bring it to the initial height. This increases the mass of the piston with sand grains. Consequently, the pressure on the gas increases and it starts getting compressed, while its volume decreases. The entire

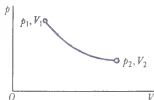


Fig. 25. A curve corresponding to
■ equilibrium process

process occurs in the reverse direction, and the temperature is maintained at a constant value due to heat exchange with the surrounding medium. The pressure of the gas in the cylinder corresponding to each position of the piston is the same as during the process of gas expansion. Consequently, with the decrease in volume, the gas in the cylinder passes through all the states which it passed during expansion, but the order is now reversed. When the gas is compressed to the volume V_0 , the piston carries all the sand grains that were earlier removed. The mass of the piston with sand is now $m(x_0) = m_0$. The entire system has thus returned to its initial position. The expansion and compression of the gas have taken place reversibly.

The gas can be irreversibly expanded, for example, by quickly removing all the sand grains at the lower position of the piston, assuming the mass of the piston without sand to be sufficiently small. Under this condition, the piston moves upwards with a large acceleration, and the gas volume correspondingly increases. In this case, the temperature varies and has different values in different parts of the cylinder volume. The gas pressure also has different values in different parts of the volume. Only the volume of the gas has a definite numerical value. The state of the gas in the cylinder cannot be characterized by any values of p and T . For this reason, the process cannot be depicted by a continuous line as in the case of reversible processes.

Sec. 17. HEAT CAPACITY

Heat capacity at a constant volume and at a constant pressure as well as their ratio are considered for an ideal gas. The discrepancy between theoretical and experimental results is analyzed. A qualitative account of the temperature dependence of heat capacity is given.

DEFINITION. When a quantity of heat δQ is supplied to a system, its temperature changes by dT . The quantity

$$C = \delta Q/dT \quad (17.1)$$

is called the heat capacity. Heat capacity is a measure of the quantity of heat required to raise the temperature of a body by one kelvin. Obviously, heat capacity depends on the mass of the body. The heat capacity per unit mass is called specific heat capacity. It is most convenient to consider a mole of the substance. Heat capacity of a mole of molecules of a substance is called the molar heat capacity. Unless otherwise stated, it is molar heat capacity that is usually meant by the heat capacity of a substance.

Heat capacity depends on conditions under which heat is

supplied to a body and its temperature changes. For example, if a quantity of heat δQ supplied to a gas makes it to expand and perform work, its temperature increases to a value which is lower than that attained by supplying the same heat δQ at $\equiv$ constant volume. Hence, according to formula (17.1), the heat capacity is higher in the case of expansion. This means that the quantity defined by (17.1) is not definite and may assume any value. To ascribe $\equiv$ definite value to the heat capacity (17.1), it is necessary to indicate the conditions mentioned above. These conditions are specified in the form of subscripts under the quantities appearing in (17.1).

The concept of heat capacity was gradually adopted in natural science in the 18th century. As early $\equiv$ 1744 G.W. Rikhman (1711-1753) established the formula for the temperature of mixtures. The theory of heat was refined and by 1780's the basic concepts of this theory were formulated in the final form. The results obtained by this time were summarized in "Mémoire Sur La Chaleur" by A.L. Lavoisier (1743-1794) and P.S. Laplace (1749-1827), published in 1783.

INTERNAL ENERGY AS A FUNCTION OF STATE. It follows from the definition of internal energy that it has quite a definite value in any state of a system. This means that the internal energy U is $\equiv$ function of state, and dU is the total differential. In further analysis, we shall more frequently use for other quantities the inverse statement: if an infinitely small quantity is $\equiv$ total differential, the corresponding function is $\equiv$ function of state.

The quantities, p , V , and T have quite definite values in any state of a system and characterize this state. Thus, dp , dV , and dT are total differentials.

HEAT CAPACITY AT CONSTANT VOLUME. This quantity is defined as

$$C_V = (\delta Q/dT)_V. \quad (17.2)$$

In thermodynamics, the ratio of infinitesimals is usually enclosed in parentheses, as in (17.2), the subscript indicating the quantity which is assumed to be constant in calculation or measurement of this ratio. It should be noted that the ratio of infinitely small quantities is, in general, not $\equiv$ derivative or a partial derivative, since, strictly speaking, infinitesimals are not total differentials.

At $\equiv$ constant volume, $dV = 0$, and hence Eq. (14.4) assumes the form

$$(\delta Q)_V = dU. \quad (17.3)$$

!

In the general case, heat capacity does not characterize the properties of $\equiv$ body. It characterizes $\equiv$ body as well as the conditions under which it is heated. Hence it does not have a definite numerical value. However, if the conditions under which the body is heated are fixed, the heat capacity becomes its characteristic property and acquires $\equiv$ certain numerical value. It is values of heat capacity that are given in tables. The most important of them are heat capacities of $\equiv$ gas at constant volume and at constant pressure.

This means that at $V = \text{const}$, δQ is a total differential. Formula (17.2) then assumes the form

$$C_V = (dU/dT)_V. \quad (17.4)$$

Therefore, C_V is a function of state, which makes this quantity very important.

HEAT CAPACITY AT CONSTANT PRESSURE. When $p = \text{const}$, Eq. (14.4) can be written in the form

$$(\delta Q)_p = dU + (p dV)_p = d(U + pV). \quad (17.5)$$

This means that $(\delta Q)_p$ is a total differential, and

$$C_p = \left(\frac{\delta Q}{dT} \right)_p \quad (17.6)$$

is a function of state.

The function of state

$$H = U + pV \quad (17.7)$$

appearing in (17.5) is called the *enthalpy*. The expression (17.6) for C_p can then be transformed as

$$C_p = \left(\frac{dH}{dT} \right)_p. \quad (17.8)$$



Heat capacity depends on the nature of a process and may change from infinite positive values to infinite negative values.

Heat capacities at constant pressure and at constant volume are functions of state.

The internal energy of an ideal gas does not depend on its volume.

The temperature independence of the heat capacity of a gas is not confirmed, for example, in experiments with molecular hydrogen.

RELATION BETWEEN HEAT CAPACITIES. We are considering a thermodynamic system characterized by three macroscopic parameters p , V , and T . These parameters are not independent. There exists a relation between them, called the *equation of state*. For an ideal gas, the equation of state has the form $pV_m = RT$. In the general case, the exact form of this dependence is unknown. Therefore, we can only state that there exists a functional dependence between these quantities, e.g.

$$p = p(T, V). \quad (17.9)$$

Of course, depending on the choice of independent variables, we can assume that $T = T(p, V)$ or $V = V(p, T)$. If we take V and T as independent variables, the internal energy of the system depends on them, i.e. $U = U(T, V)$.

Substituting the expression

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV \quad (17.10)$$

for the total differential into (14.4), we obtain

$$\delta Q = \left(\frac{\partial U}{\partial T} \right)_V dT + \left[p + \left(\frac{\partial U}{\partial V} \right)_T \right] dV. \quad (17.11)$$

Formula (17.1) for the heat capacity can then be written as

$$C = \frac{\delta Q}{dT} = \left(\frac{\partial U}{\partial T} \right)_V + \left[p + \left(\frac{\partial U}{\partial V} \right)_T \right] \frac{dV}{dT}, \quad (17.12)$$

where dV/dT on the right-hand side depends on the nature of the process. If $V = \text{const}$, this quantity vanishes, and formula (17.12) becomes (17.4) for C_V since (see (17.10)) $(dU/dT)_V = (\partial U/\partial T)_V = C_V$ for $dV = 0$. If $p = \text{const}$, (17.12) becomes the expression for the heat capacity at constant pressure:

$$\left\{ \begin{aligned} C_p &= \left(\frac{\partial U}{\partial T} \right)_V + \left[p + \left(\frac{\partial U}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_p \\ &= C_V + \left[p + \left(\frac{\partial U}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_p. \end{aligned} \right. \quad (17.13)$$

Consequently, expression (17.11) for δQ can be represented in the form

$$\delta Q = C_V dT + \left[p + \left(\frac{\partial U}{\partial V} \right)_T \right] dV. \quad (17.14)$$

RELATION BETWEEN HEAT CAPACITIES FOR AN IDEAL GAS. By definition, an ideal gas consists of particles colliding in accordance with the laws of elastic collisions. The particles are assumed to be infinitely small, and long-range forces of interaction between them are assumed to be absent. However, the particles constituting an ideal gas may themselves be complex (see Sec. 12). The energy of a complex particle is the sum of the kinetic energy of its centre of mass, and the kinetic energy of rotation and vibrations. Each degree of freedom has an energy $kT/2$ corresponding to it, which



Fig. 26. The model of a diatomic molecule

depends only on the temperature. Thus, the internal energy of an ideal gas depends only on temperature and does not depend on the gas volume. This is obvious in the case of the statistical theory of ideal gas (see Chap. 1). However, in the framework of the thermodynamic method this statement must be proved without resorting to molecular concepts. The proof is based on the second law of thermodynamics, i.e. it is shown that for a system whose equation of state coincides with the equation of state for an ideal gas, the internal energy depends only on temperature. This could not be done if we did not know the second law of thermodynamics, hence here we must be content with the existence of such a possibility.

Since $U = U(T)$ for an ideal gas, and the equation of state can be written in the form

$$V = RT/p, \quad (17.15)$$

we find

$$\left(\frac{\partial U}{\partial V}\right)_T = 0, \quad \left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{p}. \quad (17.16)$$

Substituting (17.16) into (17.13), we obtain

$$C_p = C_V + R. \quad (17.17a)$$

Relation (17.17a) for heat capacities C_p and C_V in the case of an ideal gas is called **Mayer's equation**. It should be recalled that C_p and C_V in (17.17a) correspond to a mole of gas molecules, i.e. they are molar quantities.

By dividing both sides of (17.17a) into the molar mass M of the gas, we get

$$c_p = c_V + R_0, \quad (17.17b)$$

where $c_p = C_p/M$ and $c_V = C_V/M$ are specific heat capacities at constant pressure and at constant volume, and $R_0 = R/M$ is the specific gas constant.

HEAT CAPACITY OF AN IDEAL GAS. If a particle of an ideal gas is simple, it has only three degrees of freedom of translational motion. Its energy is equal to $(3/2)kT$. If, on the other hand, such a particle is complex, it has more degrees of freedom, and hence a higher energy. For example, if a complex particle consists of two point particles, there are two possibilities. If the point particles are rigidly connected and behave like a rigid dumb-bell (Fig. 26), the complex particle has five degrees of freedom of which three are translational and two rotational (by definition, rotation about the axis passing through the point particles is impossible). In

this case, the energy of the particle is equal to $(5/2)kT$. If, in addition, the particles are not rigidly connected, and the vibrational motion along the line joining them is possible, a kinetic energy of vibration equal to $kT/2$ and a potential energy equal to $kT/2$ are additionally introduced. In other words, two additional degrees of freedom appear. Thus the total energy of a single complex particle is $(7/2)kT$. The energy of more complex particles can be calculated in a similar manner. If a complex particle has i degrees of freedom, its energy is $(i/2)kT$. There are N_A particles in a mole, and hence the internal energy of one mole of an ideal gas is equal to

$$U = (i/2) N_A kT = (i/2) RT. \quad (17.18)$$

Using formulas (17.4) and (17.17a), we obtain

$$C_V = \frac{i}{2} R, \quad C_P = \frac{i+2}{2} R. \quad (17.19)$$

DISCREPANCY BETWEEN THE SPECIFIC HEAT THEORY FOR AN IDEAL GAS AND EXPERIMENTAL RESULTS. The results given by these simple formulas are in good agreement with experiments for monoatomic and many diatomic gases at room temperature, for example, hydrogen, nitrogen, and oxygen. Their molar heat capacity turns out to be quite close to $C_V = (5/2) R$.

However, the heat capacity of diatomic chlorine gas Cl_2 is about $(6/2) R$, which cannot be explained by the specific heat theory (C_V of a diatomic molecule can in principle be either $(5/2) R$ or $(7/2) R$).

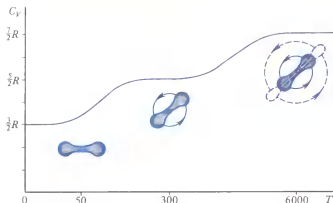
The predictions of the theory are systematically violated for triatomic gases.

The heat capacity of rigid molecules of a triatomic gas (if only they do not lie on the same straight line) must be equal to $(6/2) R$. The experimentally obtained value is somewhat higher, and this cannot be explained as due to the excitation of an additional degree of freedom. It was found experimentally that heat capacity depends on temperature, which completely contradicts the results obtained from formulas (17.19). By way of an example, let us consider in greater detail the heat capacity of molecular hydrogen. Hydrogen molecules are diatomic. Highly rarefied hydrogen gas is very close to an ideal gas and is a convenient object for the verification of the theory. For a diatomic gas, C_V is equal to either $(5/2) R$ or $(7/2) R$ and must be independent of temperature. In actual practice however, the heat capacity of molecular hydrogen depends on temperature (Fig. 27): at

$$C_V = \frac{i}{2} R$$

$$C_P = \frac{i+2}{2} R$$

Fig. 27. Experimental dependence of C_V for molecular hydrogen on the temperature T



a low temperature (about 50 K) its heat capacity is $(3/2)R$, while at room temperature, it is $(5/2)R$, and at very high temperatures the heat capacity becomes equal to $(7/2)R$. Thus, at low temperatures, a molecule of hydrogen behaves as a point particle without any internal motions. The molecule behaves like a rigid dumb-bell at normal temperature and performs rotational motion in addition to the translational one. At very high temperatures, these motions are supplemented by the vibrational motions of the atoms constituting the molecule. It appears as if a change in temperature results in the inclusion (or exclusion) of different degrees of freedom: at low temperatures, only the translational degrees of freedom are included; the rotational degrees of freedom come into play when the temperature is increased, while a further increase in temperature leads to the introduction of the vibrational degrees of freedom.

However, the transition from one type of motion to another does not occur abruptly at a certain temperature, but takes place slowly over a certain interval of temperature. This is due to the fact that at a certain temperature it becomes possible for the molecules to go over from one type of motion to another, although this possibility is not realized at once by all the molecules but just by some of them. As the temperature changes, more and more molecules go over to the other type of motion, and hence the heat capacity curve changes smoothly over a certain interval of temperatures.

At a sufficiently low temperature, the motion of hydrogen molecules between collisions is similar to the translatory motion of solids:



?

1. Which physical considerations lead to the conclusion that the heat capacity of an ideal gas at constant pressure is larger than the heat capacity at constant volume?
2. Does heat capacity depend on the potential energy of interaction between molecules in the general case?
3. Does the heat capacity of a gas depend on the gravitational field in which the gas is?

As the temperature is increased, the rotational degrees of freedom appear, and the pattern of motion of molecules somewhat changes in that a molecule rotates during its translatory motion between collisions:



Vibrational degrees of freedom appear upon a further increase in temperature, and the molecular motion becomes even more complicated. This is so because during the translational motion the atoms comprising a molecule vibrate about the axis, thus changing their orientation in space:



The classical theory was not able to explain the dependence of heat capacity on temperature. A quantitative account of the dependence which is described by quantum-mechanical laws of motion can be given only by solving quantum-mechanical equations of motion. The physical significance of the process can, however, be understood even without solving these equations.

QUALITATIVE EXPLANATION OF THE TEMPERATURE DEPENDENCE OF THE HEAT CAPACITY OF MOLECULAR HYDROGEN. A striking feature of the motion of microscopic particles is that they can have only discrete values of energy. Whenever the motion of a particle is restricted to a finite region, it can assume only a discrete set of values. As this region is extended, the distance between the energy levels decreases, and for a sufficiently large region of motion, the energy spectrum of a particle can be considered as continuous with a fairly high degree of accuracy, although in principle it remains discrete. Another case when this spectrum is practically continuous involves particles with very high energies. In this case, the distance between the energy levels is negligibly small in comparison with the energy. The discrete energy spectrum of a particle is obtained by solving the quantum-mechanical equations of motion.

We shall describe the result of the solution for a diatomic hydrogen molecule. The allowed energy values for the translational motion are practically assumed to be continuous, since the region of motion for a mole of rarefied gas is sufficiently large. The energy of vibrational and rotational motions is quantized. In other words, only

a discrete set of the rotational and vibrational energy values are possible rather than any arbitrary values. The vibrational energy spectrum has an especially simple form:

$$E_n = \hbar\omega (n + 1/2), \quad (17.20)$$

where $\hbar\omega$ is determined by the atomic masses and the coefficient of elasticity. The energy $E_0 = \hbar\omega/2$ is minimum. In other words, the laws of motion are such that the particle is not in a state of rest. The allowed vibrational energy levels of the molecule, which lie above the zero level, are separated by equal intervals $\hbar\omega$.

The rotational energy of a molecule is about 100 times smaller than its vibrational energy. In other words, the rotational motion is slower than the vibrational motion. The energy spectrum of the rotational motion of a hydrogen molecule has the form

$$E_n = q_1 n(n + 1), \quad (17.21)$$

where $q_1 = \hbar^2/(2J_0)$, J_0 being the moment of inertia of the molecule with respect to the rotational axes (in the present case, the moments are identical relative to the axes).

There are two types of hydrogen molecules which differ in the orientation of the spin of their nuclei. Spin characterizes the internal angular momentum of an elementary particle. It appears as though the elementary particle is rotating. In actual practice, the spin of an elementary particle cannot be explained by rotation since for a quantitative agreement with the experiment it would be necessary to admit that the linear velocities on the "surface" of an elementary particle are higher than the velocity of light, which is impossible. Hence spin must be considered as a fundamental quantity, which is by nature inherent in particles. The spin of a nucleus is equal to the sum of the spins of the elementary particles constituting it, viz. the protons and the neutrons. In the case of a hydrogen molecule, we are speaking only of the proton spins. For parahydrogen molecules (in which the spins are antiparallel), n in (17.21) can assume values $n = 0, 2, 4, \dots$, while for orthohydrogen (in which the spins are parallel), $n = 1, 3, 5, \dots$. The number of parahydrogen and orthohydrogen molecules in the total number of hydrogen molecules is $1/4$ and $3/4$ respectively.

The vibrational levels are much more closely-spaced than the rotational levels. The distance between the lowest level and the first excited level plays a very important role. Thus, in the case of paramolecules, it is the distance between the levels $E_0 = 0$ and E_2 , i.e. $(\Delta E)_0 = 5q_1$, while in the case of

orthomolecules it is the distance between E_1 and E_3 , i.e. $(\Delta E)_1 = 10q_1$.

The collisions between molecules lead to an exchange of energy between the translational, rotational, and vibrational degrees of freedom. At very low temperatures, when $kT \ll 5q_1$, the vibrational or even the rotational degrees of freedom cannot be excited since the energy imparted to them during a collision is insufficient. Consequently, the molecule moves with minimum vibrational energy (zero-point vibrational energy) and with minimum rotational energy (equal to $E_0 = 0$ for parahydrogen and $E_1 = 2q_1$ for orthohydrogen). Molecules behave like particles without any internal degrees of freedom, and thus have only three degrees of freedom. The heat capacity of such a gas is $3R/2$. With increasing temperature, when the translational energy becomes sufficient for exciting the rotational levels, the molecule starts behaving like a complex particle with five degrees of freedom. Such a behaviour is observed for $kT \geq q_1$. The temperature at which the rotational degrees of freedom appear is taken to be equal to

$$T_{\text{rot}} = q_1/k = h^2/(2J_0k). \quad (17.22)$$

Above the temperature T_{rot} , the heat capacity of a diatomic gas is equal to $5R/2$ right up to

$$T_{\text{vib}} = h\omega/k. \quad (17.23)$$

At this stage, the vibrational degrees of freedom appear and the heat capacity becomes equal to $7R/2$.

For hydrogen $T_{\text{rot}} = 85.5$ K and the heat capacity of molecular hydrogen under normal conditions is $5R/2$. Vibrational degrees of freedom appear in hydrogen at $T_{\text{vib}} = 6410$ K. However, a considerable fraction of molecules dissociates into atoms at such a high temperature. The actually observed value of heat capacity is composed of the specific heat of molecular and atomic hydrogen and is equal to $7R/2$. Thus, the behaviour of heat capacity of molecular hydrogen as a function of temperature is completely described by quantum mechanics. It also provides a satisfactory quantitative explanation for the behaviour of the heat capacity. In order to calculate the mean values of the rotational and vibrational energies of molecules, we must know the distribution of the molecules over these energies. This cannot be accomplished with the help of the Gibbs distribution. Calculations are made by using Bose-Einstein distribution.

The values of T_{rot} and T_{vib} for other diatomic molecules are lower than for molecular hydrogen. For N_2 , $T_{\text{rot}} =$

$= 2.86 \text{ K}$ and $T_{\text{vib}} = 3340 \text{ K}$, while for O_2 , the corresponding values are 2.09 K and 2260 K . The decrease in the values of T_{rot} and T_{vib} is due to an increase in the mass of the atoms constituting the molecules.

Example 17.1. Find the specific heat of oxygen at constant pressure and high temperature with the help of classical theory.

At high temperature, the rotational degrees of freedom are excited and hence the number of degrees of freedom of an oxygen molecule is $i = 5$. The molar heat capacity $C_p = (i + 2)R/2$. The molar mass of oxygen is $M = 0.032 \text{ kg/mole}$. The specific heat is then equal to

$$c_p = (i + 2)R/(2M) = [7 \times 8.31/(2 \times 0.032)] \text{ J/(kg} \cdot \text{K)} \\ = 0.909 \text{ kJ/(kg} \cdot \text{K)}.$$

Sec. 18. PROCESSES IN IDEAL GASES

Isobaric, isochoric, isothermal, and adiabatic processes are considered. The adiabatic and polytropic equations are derived.

ISOBARIC PROCESS. This is a process occurring at constant pressure: $p = \text{const}$ (Fig. 28). The temperatures at the points (p_1, V_1) and (p_2, V_2) are determined by the equation of state and are equal to $T_1 = p_1 V_1 / R$ and $T_2 = p_2 V_2 / R$ respectively. In order to maintain a constant pressure, heat must be supplied to the system as the volume increases. The work done in this process is defined by the integral

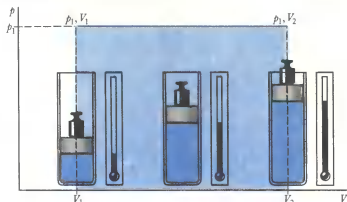
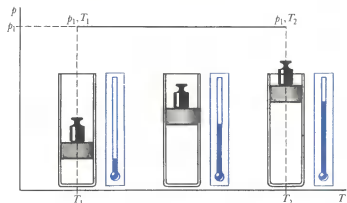
$$A = \int_{(1)}^{(2)} p_1 dV = p_1 (V_2 - V_1). \quad (18.1)$$

In the p, V coordinates, the work is equal to the area bounded by the curve depicting the process, the V -axis, and the vertical lines passing through the initial and the final points. This area is shaded in Fig. 28.

In the p, T coordinates also, the process is represented by a straight line (Fig. 29). The expression for work in terms of these variables has the form

$$A = \int_{(1)}^{(2)} p_1 dV = \int_{(1)}^{(2)} p_1 \frac{R}{p_1} dT = R(T_2 - T_1). \quad (18.2)$$

Both these representations are equivalent. We can formally go over from one of these to the other by using the equation of state. Hence, as a rule, the processes are described by using one of these representations, preferably in the p, V coordinates.

Fig. 28. Isobaric process in the p, V coordinatesFig. 29. Isobaric process in the p, T coordinates

ISOCHORIC PROCESS. This is a process which occurs at a constant volume: $V = \text{const}$ (Fig. 30). In this process, the work is equal to

$$A = \int_{(1)}^{(2)} p dV = 0. \quad (18.3)$$

ISOTHERMAL PROCESS. This is a process carried out at a constant temperature: $T = \text{const}$ (Fig. 31). In this case, the work is given by

$$A = \int_{(1)}^{(2)} p dV = RT \int_{V_1}^{V_2} \frac{dV}{V} = RT \ln \frac{V_2}{V_1}. \quad (18.4)$$

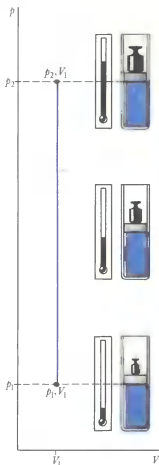


Fig. 30. Isochoric process in the p , V coordinates

The internal energy of an ideal gas does not change in this process since $T = \text{const}$, and hence $dU = 0$. Consequently, from the first law of thermodynamics it follows that $\delta Q = \delta A$. This means that the entire heat supplied from outside in an isothermal process is spent to accomplish work.

ADIABATIC PROCESS. This is a process in which there is no heat exchange with the ambient. Hence, the first law of thermodynamics has the following form for this process:

$$C_V dT + p dV = 0. \quad (18.5)$$

Obviously, when $dV > 0$, $dT < 0$. Therefore, the work done by the gas during expansion is performed at the expense of its internal energy. When $dV < 0$, $dT > 0$, and hence the work done on the gas leads to an increase in its internal energy (and temperature).

The adiabatic equation is a relation connecting the parameters in adiabatic process. Let us derive this equation.

The equation for ideal gases gives the following expression for T :

$$T = pV / (C_p - C_V), \quad (18.6)$$

where the Mayer equation $R = C_p - C_V$ is used. By dividing Eq. (18.5) by $C_V T$, we find

$$\frac{dT}{T} + (\gamma - 1) \frac{dV}{V} = 0, \quad (18.7)$$

where $\gamma = C_p / C_V$ is the adiabatic exponent.

Integrating and taking antilogarithm of this equation, we obtain the adiabatic equation in terms of T and V :

$$TV^{\gamma-1} = \text{const.} \quad (18.8)$$

In order to go over to variables p and V , we exclude temperature from this equation by using the equation of state $T = pV/R$. This gives

$$pV^{\gamma} = \text{const.} \quad (18.9a)$$

Similarly, we obtain

$$T^{\gamma} p^{1-\gamma} = \text{const.} \quad (18.9b)$$

In accordance with Eq. (17.19), we get $\gamma = (i + 2)/i$. Hence, for monoatomic gases that are sufficiently close to ideal gas, $i = 3$, and $\gamma = 1.66$. This is in good agreement with

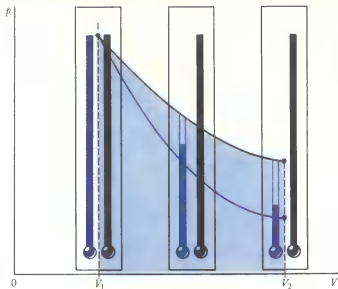


Fig. 31. Isothermal (black curve) and adiabatic (blue curve) processes

experiments. For example, for helium $\gamma = 1.66$. For diatomic gases in which only rotational degrees of freedom are excited, $i = 5$, and hence $\gamma = 1.40$. This is also in accord with experiments. For example, for oxygen, nitrogen, and air $\gamma = 1.40$, while for hydrogen $\gamma = 1.41$.

WORK IN AN ADIABATIC PROCESS. The general formula for work gives

$$A = \int_{(1)}^{(2)} p dV = p_1 V_1 \int_{V_1}^{V_2} \frac{dV}{V^\gamma} = \frac{p_1 V_1}{1-\gamma} (V_2^{-\gamma+1} - V_1^{-\gamma+1}) = \frac{RT_1}{\gamma-1} \left[1 - \left(\frac{V_1}{V_2} \right)^{\gamma-1} \right], \quad (18.10)$$

where $p_1 V_1 = RT_1$.

Considering that $(V_1/V_2)^{\gamma-1} = T_2/T_1$, we can transform Eq. (18.10) as follows:

$$A = R(T_1 - T_2)/(\gamma - 1). \quad (18.11)$$

When a gas expands from the state p_1, V_1 to a certain volume V_2 , the work done during an adiabatic process is less

!

Processes in a gas do not occur independently. They proceed due to external conditions imposed on the gas. The gas as if is made to pass through a certain sequence of equilibrium states. Left to itself, an ideal gas can do nothing but dissipate in infinite space. A real gas is different: it is sufficient to recall that once upon a time the Universe was apparently made up of matter in the gaseous state only.

than during an isothermal process (Fig. 31). This can be explained by the fact that the gas is cooled during the adiabatic process, while the temperature remains constant during the isothermal process due to the heat supplied by a thermostat. Hence, in an isothermal process the pressure of the gas decreases upon expansion only due to a decrease in the density of the gas. In an adiabatic process, the pressure decreases due to a decrease in the density and the mean kinetic energy, i.e. temperature.

The adiabatic equation can be obtained from simple kinetic considerations. We direct the X -axis along the axis of a cylinder with adiabatic walls and piston. This means that the impacts of molecules against the walls and the piston are perfectly elastic. Suppose that the piston moves with a negligibly small velocity u thus changing the volume of the gas. The kinetic energy of a molecule is not conserved during an impact with the moving piston and can either increase or decrease. Clearly, only molecules moving towards the piston can strike it. If the volume increases, the molecules catch up with the piston, and if it decreases, they meet the piston. The collisions with the piston take place as if it had an infinite mass. From the laws of conservation of energy and momentum during collisions, we find that the absolute value of the x th component of a particle velocity changes by $2u$ as a result of the collision, increasing during compression and decreasing during expansion.

Hence the kinetic energy of a molecule changes as a result of a collision by

$$\Delta W = (m/2)(|v_x| \pm 2u)^2 - mv_x^2/2 = \pm 2m|v_x|u, \quad (18.12)$$

where the second-order term in u has been neglected.

For the sake of definiteness, we shall assume that the piston moves along the positive direction of the X -axis, thus increasing the volume. Then, taking the signs into account, we can write

$$\Delta W = -2mv_x^{(+)}u, \quad (18.13)$$

where $v_x^{(+)}$ indicates that we consider only the molecules moving in the positive direction of the X -axis and catching up with the piston. Only the x -component of the velocity changes during a collision between a molecule and the piston, other components remaining unchanged. Hence the kinetic energy of the molecule also changes only as a result of the change in the x -component of the velocity.

In accordance with (8.31), the number of molecules impinging upon the piston with area S at a velocity lying

between v and $v + dv$ during time dt is equal to

$$dn = (n/V)f(v)dv v_x^{(+)}S dt,$$

where $f(v)$ is the Maxwell distribution. Taking into account formula (18.13), we can write the following expression for the change in the kinetic energy of molecules contained in the cylinder:

$$dU = -2mv_x^{(+)}u dn = -2m(n/V)Su dt f(v)(v^{+})^2 dv.$$

Note that $Su dt = S dx = dV$ is the change in the cylinder volume due to the motion of the piston. Hence, the total change in the internal energy of the gas in the cylinder during adiabatic increase of its volume is

$$dU = -2m(n/V)dV \int f(v)(v^{+})^2 dv, \quad (18.14)$$

where the integral (see (10.2)) comprises only the molecules with the positive x -component of their velocity. Taking (10.2) into account, this equation assumes the form

$$dU = -(n/V)dV kT. \quad (18.15)$$

For a gas with i degrees of freedom, $U = nikT/2$. Using this expression in Eq. (18.15), we get

$$(i/2)dT/T = -dV/V. \quad (18.16)$$

Considering that $(i/2)dT/T = d(\ln T^{i/2})$ and $dV/V = d \ln V$, we find

$$d \ln (T^{i/2} V) = 0.$$

Consequently, the adiabatic equation has the form

$$T^{i/2} V = \text{const.}$$

This equation can be given a more conventional form by raising it to the power $2/i$:

$$TV^{2/i} = TV^{\gamma-1} = \text{const}, \quad (18.17)$$

since $\gamma = (i+2)/i = 1 + 2/i$. This example illustrates how thermodynamic relations can be obtained by using the methods of kinetic theory.

POLYTROPIC PROCESS. All the processes considered above have a property in common, viz. they occur at constant heat capacity. This immediately follows from the analytic form of the conditions under which a process takes place. For isochoric and isobaric processes, heat capacities are equal to C_V and C_p respectively, for isothermal processes

($dT=0$) the heat capacity is equal to $\pm\infty$, while for adiabatic processes ($\delta Q=0$) the heat capacity is 0. Processes in which heat capacity is a constant quantity are called polytropic. Isobaric, isochoric, isothermal, and adiabatic processes are particular cases of the polytropic process.

POLYTROPIC EQUATION. The first law of thermodynamics has the following form for processes in which C is constant:

$$C dT = C_V dT + p dV. \quad (18.18)$$

Transforming this equation as we did with Eq. (18.5) in order to obtain Eq. (18.7), we find

$$\frac{dT}{T} + \frac{C_p - C_V}{C_V - C} \frac{dV}{V} = 0. \quad (18.19)$$

Integrating this equation, we get

$$TV^{n-1} = \text{const}, \quad (18.20)$$

where $(C_p - C_V)/(C_V - C) = n - 1$.

This is the polytropic equation in terms of T and V . Using the expression $T = pV/R$ to eliminate T from this equation, we obtain

$$pV^n = \text{const}, \quad (18.21)$$

where $n = (C - C_p)/(C - C_V)$ is the polytropic exponent.

Obviously, for $C=0$ and $n=\gamma$, we obtain the adiabatic equation, for $C=\infty$ and $n=1$, the equation of isotherm, for $C=C_p$ and $n=0$ the equation of isobar, and for $C=C_V$ and $n=\pm\infty$ the equation of isochor.

Example 18.1. Helium, whose initial temperature $T_0 = 400$ K and volume $V_0 = 10$ l, expands adiabatically. During this expansion, its pressure drops from $p_0 = 5 \times 10^6$ to $p = 2 \times 10^5$ Pa. Find the volume and temperature of helium in the final state.

For an adiabatic expansion, we have

$$pV^\gamma = p_0V_0^\gamma,$$

where $\gamma = C_p/C_V = 5/3 = 1.66$ in the case of helium. Hence, the final volume is

$$V = (p_0/p)^{1/\gamma} V_0 = (25)^{0.6} 10 \text{ l} = 69 \text{ l}.$$

Now, we write the equations for an ideal gas in the initial and the final states:

$$p_0V_0 = \nu RT_0, \quad pV = \nu RT.$$

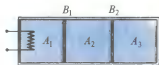


Fig. 32. A cylinder with n gas, separated into three regions by partitions B_1 and B_2

Dividing the left- and right-hand sides of these equations termwise, we obtain

$$T = \frac{pV}{p_0 V_0} T_0 = \frac{2 \cdot 69}{50 \cdot 10} 400 \text{ K} = 110.4 \text{ K}.$$

Example 18.2. A cylinder with adiabatic walls is divided into three parts A_1 , A_2 , and A_3 (Fig. 32) by a heat-insulating piston B_1 and diathermic piston B_2 . The pistons can slide along the cylinder walls without friction. Each part of the cylinder contains 0.1 mole of an ideal diatomic gas. At first, the gas pressure in all three parts is $p_0 = 10^5$ Pa and the temperature $T = 300$ K. Then the gas in part A_1 is heated slowly until the gas temperature in portion A_3 becomes $T_3 = 340$ K. Find the pressure, temperature, volume, and the change in the internal energy of the gas in the final state for each part, and the total energy which was supplied to the gas in A_1 during heating.

In equilibrium, the pressure of the gas in all parts will be the same ($p_1 = p_2 = p_3$). Moreover, since the piston B_2 is diathermic, the temperatures in parts A_2 and A_3 must be equal ($T_2 = T_3 = 340$ K). As the masses of the gas in these parts are equal, the volumes V_2 and V_3 must also be the same. According to Eq. (18.9a), for an adiabatic reversible change in the state of the gas in sections A_2 and A_3 we have $p_3 = p_2 = p_0 (T_2/T_0)^{\gamma/(\gamma-1)}$. In the initial state, the volumes of the three sections are the same and equal to $V_0 = 0.1 RT_0/p_0$, while the final volumes of sections A_2 and A_3 are equal to $V_2 = V_3 = 0.1 RT_2/p_2$, or

$$V_2 = V_3 = (0.1 RT_0/p_0) (T_0/T_2)^{1/(\gamma-1)}.$$

For n diatomic gas, $\gamma = (i+2)/i = 7/5$, and hence

$$V_2 = V_3 = \frac{8.31 \cdot 0.1 \cdot 300}{10^5} \left(\frac{300}{340} \right)^{5/2} \text{ m}^3 = 1.8231 \cdot 10^{-3} \text{ m}^3.$$

The pressure $p_2 = 0.1 RT_2/V_2 = 8.31 \times 0.1 \times 340 / (1.8231 \times 10^{-3}) \text{ Pa} = 1.55 \times 10^5 \text{ Pa}$.

The volume V_1 can be found from the condition that the total volume of the cylinder remains constant:

$$\begin{aligned} V_1 &= 3V_0 - (V_2 + V_3) \\ &= 3 \cdot 0.1 RT_0/p_0 - (2 \cdot 0.1 RT_0/p_0) (T_0/T_2)^{1/(\gamma-1)}, \end{aligned}$$

$$pV^n = \text{const}$$

$$n = \frac{C - C_p}{C - C_v}$$

whence

$$\begin{aligned} V_1 &= 3 \cdot 8.31 \cdot 0.1 \cdot 300 \cdot 10^{-5} \text{ m}^3 - 2 \cdot 1.8231 \cdot 10^{-3} \text{ m}^3 \\ &= 3.833 \cdot 10^{-3} \text{ m}^3. \end{aligned}$$

For the temperature T_1 , we get

$$\begin{aligned} T_1 &= p_1 V_1 / (R \cdot 0.1) = p_2 V_1 / (R \cdot 0.1) \\ &= T_0 [3 (T_2 / T_0)^{\gamma/(\gamma-1)} - 2 T_2 / T_0] \\ &= [1.55 \cdot 10^5 \cdot 3.8328 \cdot 10^{-3} / (8.31 \cdot 0.1)] \text{ K} = 715 \text{ K}. \end{aligned}$$

The internal energy changes by $\Delta U = 0.1 C_V \Delta T = (0.1 \times \times i/2) R \Delta T$, where i is the number of degrees of freedom of gas molecules. This gives $\Delta U_1 = 8.31 \times \times 0.1 (715 - 300) (5/2) \text{ J} = 862.2 \text{ J}$, $\Delta U_2 = \Delta U_3 = 8.31 \times \times 0.1 (340 - 300) (5/2) \text{ J} = 83.1 \text{ J}$. From the law of conservation of energy it follows that the total energy supplied to the gas in A_1 is $\Delta U = \Delta U_1 + \Delta U_2 + \Delta U_3 = = (862.2 + 83.1 + 83.1) \text{ J} = 1028.4 \text{ J}$.

Example 18.3. Solve the problem formulated in Example 18.2 assuming that the pistons B_1 and B_2 are adiabatic.

In this case, the state of the gas in sections A_2 and A_3 changes in accordance with the adiabatic equations $T_0^{\gamma} p_0^{1-\gamma} = T_2^{\gamma} p_2^{1-\gamma}$ and $T_0^{\gamma} p_0^{1-\gamma} = T_3^{\gamma} p_3^{1-\gamma}$. Since we have $p_1 = = p_2 = p_3$ as before, $T_2 = T_3$, i.e. the state of the gas in sections A_2 and A_3 is the same as in Example 18.2.

Sec. 19. ENTROPY OF IDEAL GAS

The entropy of an ideal gas is defined and its physical meaning is elucidated. The change in entropy is calculated for different processes. The specific nature of heat in form of energy is discussed.

DEFINITION. Let us divide by T both sides of the equation describing the first law of thermodynamics. We get

$$\frac{\delta Q}{T} = C_V \frac{dT}{T} + \frac{p}{T} dV. \quad (19.1)$$

Substituting $p/T = R/V$ into this equation and considering that $dT/T = d \ln T$ and $dV/V = d \ln V$, we obtain

$$\delta Q/T = d(C_V \ln T + R \ln V). \quad (19.2)$$

The right-hand side of this equation is a total differential. Consequently, its left-hand side $\delta Q/T$ is also a total differential. The function of state whose differential is $\delta Q/T$ is

called the **entropy** and denoted by S . Hence,

$$dS = \delta Q/T. \quad (19.3)$$

It should be noted that the validity of this expression for the total differential of entropy was proved above only for reversible processes in an ideal gas. Later, this expression will be extended for reversible processes in systems differing from an ideal gas. In the case of nonequilibrium, irreversible processes, this representation of dS in terms of δQ and T is incorrect. It should also be emphasized that formula (19.3) defines the difference in entropies rather than its absolute value. This formula can be used to calculate the change in entropy caused by a transition from one equilibrium state to another, but it does not give the value of entropy in each state. In other words, this formula defines the entropy to within an arbitrary additive constant.

PHYSICAL MEANING OF ENTROPY. Let us use formula (19.2) for calculating the change in entropy during an isothermal process ($T = \text{const}$) in which the energy state of a gas remains unchanged and possible changes in the parameters are only due to changes in the volume. In this case, we have

$$dS = R d \ln V, \quad (19.4)$$

and hence

$$\int_{(1)}^{(2)} dS = R \int_{(1)}^{(2)} d \ln V. \quad (19.5)$$

Evaluating the integrals, we get

$$S_2 - S_1 = R (\ln V_2 - \ln V_1) = R \ln (V_2/V_1). \quad (19.6)$$

In order to transform the expression on the right-hand side further, we must take into account the relation between the volume occupied by the gas in an equilibrium state and the number of spatial microscopic states of the gas particles, defined by formula (5.6). The number of particles in a mole of a gas is determined by the Avogadro constant N_A . Hence for the volumes V_1 and V_2 appearing in (19.6), formula (5.6) becomes

$$\Gamma_{01} = \frac{N_1!}{(N_1 - N_A)!}, \quad \Gamma_{02} = \frac{N_2!}{(N_2 - N_A)!}, \quad (19.7)$$

where $N_1 = V_1/l^3$, $N_2 = V_2/l^3$, and $l = 10^{-10}$ m. Using the

Stirling formula (5.11), we obtain

$$\frac{\Gamma_{02}}{\Gamma_{01}} = \frac{N_2! (N_1 - N_A)!}{N_1! (N_1 - N_A)!} \approx \frac{(N_2/e)^{N_2} [(N_1 - N_A)/e]^{N_1 - N_A}}{(N_1/e)^{N_1} [(N_2 - N_A)/e]^{N_2 - N_A}}. \quad (19.8)$$

We assume that the gas is not very compressed, i.e. $N_1 \gg N_A$ and $N_2 \gg N_A$. Hence, in the square brackets on the right-hand sides we can ignore N_A in comparison with N_2 and N_1 . Then (19.8) becomes

$$\frac{\Gamma_{02}}{\Gamma_{01}} \approx \left(\frac{N_2}{N_1}\right)^{N_A} = \left(\frac{V_2}{V_1}\right)^{N_A}. \quad (19.9)$$

Taking logarithms of both sides, we find

$$\ln \frac{V_2}{V_1} = \frac{1}{N_A} \ln \frac{\Gamma_{02}}{\Gamma_{01}}. \quad (19.10)$$

Substituting this expression into formula (19.6), we obtain

$$S_2 - S_1 = \frac{R}{N_A} \ln \frac{\Gamma_{02}}{\Gamma_{01}} = k \ln \Gamma_{02} - k \ln \Gamma_{01}, \quad (19.11)$$

where $R/N_A = k$ is Boltzmann's constant.

The form of this expression implies that the entropy S is determined by the logarithm of the number of microscopic states through which a given macroscopic state is realized, i.e.

$S = k \ln \Gamma.$

(19.12)

This formula expresses the Boltzmann entropy hypothesis. The above arguments do not prove this formula in the general form, since it is valid for (1) an ideal gas and for spatial microscopic states and (2) reversible processes. Formula (19.12) can in principle be supplemented by an arbitrary constant which was put equal to zero without any proof.

However, there are all grounds to suppose that formula (19.12) is valid in the general case as well. First of all (see Sec. 7), it is clear that the number of microscopic states through which a macroscopic state is realized is the most important function of state. And since the concept of the number of microscopic states is applicable not only to an ideal gas and equilibrium states, but also to arbitrary statistical systems, it is natural to conclude that the

!

In any reversible process, the entropy of the system changes under the effect of the external conditions affecting the system. The effect of the external conditions on entropy consists in the following. The external conditions determine the microscopic states attainable by the system as well as their number. Within the limits of the attainable microscopic states, the system attains the equilibrium state while the entropy attains the corresponding value. Consequently, the value of the entropy follows the change in the external conditions and attains its maximum value in conformity with the external conditions.

Boltzmann entropy hypothesis is of general significance. This is indeed found to be true.

Formula (19.12) provides a very clear visual interpretation of entropy. The more ordered a system, the lower the number of microscopic states through which a macroscopic state is realized. Let us assume, for example, that all the molecules are fixed at definite positions. In this case there is only one microscopic state and the corresponding entropy value is equal to zero. The larger the number of microscopic states, the more disordered a system. It can therefore be stated that the entropy of a system is a measure of its order. In the equilibrium state the entropy attains its maximum value, since the equilibrium state is the most probable state compatible with fixed conditions and is thus the macroscopic state accomplished through the largest number of microscopic states. Obviously, a system which is represented through itself moves towards the equilibrium state. In other words, the entropy of a system represented by itself must increase. This is one of the formulations of the second law of thermodynamics (see Sec. 22).

CALCULATION OF THE ENTROPY VARIATION IN PROCESSES OCCURRING IN AN IDEAL GAS. This is carried out in accordance with formula (19.2) taking formula (19.3) into account:

$$dS = d(C_V \ln T + R \ln V). \quad (19.13)$$

The change in the entropy in an isothermal process is given by formula (19.6): the entropy increases with increasing volume and decreases with decreasing volume. This result can be easily understood without calculations: an increase in volume indicates an increase in the number of positions which can be occupied by a fixed number of particles. Hence the number of different possible distributions over these places increases. In other words, the number of spatial microscopic states increases, i.e. the entropy increases.

For isochoric processes ($dV = 0$), we have

$$S_2 - S_1 = C_V \ln (T_2 / T_1), \quad (19.14)$$

i.e. the entropy increases with temperature. This result can be expressed as follows: the mean energy of particles increases with temperature, and hence the number of possible energy states also increases.

For adiabatic processes, we obtain from (19.13)

$$S_2 - S_1 = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}, \quad (19.15)$$

!

Entropy is defined as the logarithm of the number of microscopic states through which a macroscopic state is attained.

Entropy attains its maximum value in the equilibrium state, since the thermodynamic probability in the equilibrium state is maximum. Consequently, the entropy of an isolated system which is represented by itself will increase until it attains its maximum value compatible with the conditions.

and since

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}, \quad \gamma = C_p/C_V,$$

we have $\ln(T_2/T_1) = (\gamma - 1) \ln(V_1/V_2) = -(\gamma - 1) \ln(V_2/V_1)$. Formula (19.15) then assumes the form

$$S_2 - S_1 = \left[-C_V \left(\frac{C_p}{C_V} - 1 \right) + R \right] \ln \frac{V_2}{V_1} = 0, \quad (19.16)$$

since $-C_p + C_V + R = 0$ (in accordance with the Mayer equation (17.17a)). Thus, in **adiabatic reversible processes the entropy does not change**. The reason behind this is not hard to understand. During an adiabatic expansion of a gas, the entropy increases due to an increase in the volume. However, since the temperature decreases in this case, the entropy drops and these two tendencies completely compensate each other.

HEAT AS A FORM OF ENERGY. We can now answer the question raised above as to why an infinitely small amount of heat δQ is not a total differential. This is so because the quantity of heat is characterized not only by the energy but also by another quantity associated with it. This is the entropy which can be quantitatively represented by formula (19.3). Thus two quantities of heat δQ_1 and δQ_2 which correspond to the same energy have entirely different entropies: the quantity of heat associated with the higher temperature has a lower entropy than the quantity corresponding to the lower temperature. Since the entropy is a function of state, the same quantity of heat may cause entirely different changes in the state of a system.

Example 19.1. Express the work done by an ideal gas during isothermal expansion in terms of the change in entropy.

The work done by ν moles upon isothermal expansion from V_0 to V at $T_0 = \text{const}$ is equal to

$$A = \int_{V_0}^V p dV = \nu R T_0 \int_{V_0}^V dV/V = \nu R T_0 \ln(V/V_0). \quad (19.17)$$

In accordance with (19.13), the change in entropy in this case will be

$$\Delta S = \int_{(1)}^{(2)} dS = S_2 - S_1 = \nu R [\ln V]_{V_0}^V = \nu R \ln(V/V_0), \quad (19.18)$$

since $dT = 0$. With the help of (19.18), formula (19.17) can be

reduced to the form

$$A = T_0 (S_2 - S_1) = T_0 \Delta S. \quad (19.19)$$

Example 19.2. Two vessels of different volumes contain molecules of the same gas at different temperatures T_1 and T_2 . The vessels are then connected with each other, the gases are mixed, and the system attains the equilibrium state. Find the change in entropy during this process.

The reversible process through which the system can be transformed from the initial to the final state involves the isobaric expansion of each gas to the total volume. In this case the temperature of each of the gases changes to the final temperature $(T_1 + T_2)/2$. Consequently, the change in entropy for each gas will be given by

$$\Delta S_1 = \nu C_p \int_{T_1}^{(T_1+T_2)/2} dT/T = \nu C_p \ln \frac{T_1 + T_2}{2T_1},$$

$$\Delta S_2 = \nu C_p \ln \frac{T_1 + T_2}{2T_2},$$

where C_p is the molar heat capacity at constant pressure. The total change in entropy will be equal to

$$\Delta S = \Delta S_1 + \Delta S_2 = \nu C_p \ln \frac{(T_1 + T_2)^2}{4T_1 T_2} = 2\nu C_p \ln \frac{T_1 + T_2}{2\sqrt{T_1 T_2}}.$$

Sec. 20. CYCLIC PROCESSES

The work done during a cycle and the efficiency are considered. Different formulations of the second law of thermodynamics are discussed and their equivalence is proved. The operation of refrigerators and heat engines is described.

DEFINITION. A cyclic process is one in which the initial and final positions coincide. A cycle is represented in the state diagram by a closed curve (Fig. 33). A cycle can be completed in the clockwise or anticlockwise direction. Hence, wherever necessary, arrows are used to indicate the direction along which a cycle proceeds. Different parts of a closed curve representing a cycle can also be expressed by letters. For example, L_1 and L_2 denote different lines connecting states 1 and 2.

WORK OF A CYCLE. Starting from the state 1, we shall complete a cycle by moving along the line representing it in the clockwise direction. The work done in this case is equal to

$$A = \int_{L_1^{(1)}}^{(2)} p dV + \int_{L_2^{(2)}}^{(1)} p dV. \quad (20.1)$$

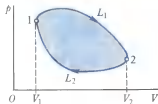


Fig. 33. A cycle. The work of the cycle is determined by the area bounded by the curve depicting the cycle

The first integral in this equation is equal to the work done during the process shown by the line L_1 which represents a transition from state 1 to state 2. It is equal to the area enclosed between this curve, the V -axis, and the segments (1, V_1) and (2, V_2). The second integral has a negative value ($dV < 0$) and is equal to the work which must be performed in order to return the system from state 2 to state 1 through the process represented by the curve L_2 . The absolute value of this integral is equal to the area bounded by the curve L_2 , the V -axis, and the segments (1, V_1) and (2, V_2), but with the negative sign. Consequently, the work of the cycle, which is equal to the sum of the two integrals in (20.1), is given by the area bounded by the closed curve representing the cycle. The definitions of a cycle, the work of the cycle, and other concepts considered in this section are not associated with an ideal gas and are of a general nature. If both sides of the equation

$$\delta Q = dU + p dV,$$

representing the first law of thermodynamics are integrated over the cycle under consideration, we obtain

$$\oint \delta Q = \oint dU + \oint p dV. \quad (20.2)$$

In this equation, the integration is carried out over the cycle. The integral of a quantity which is not a total differential means that it is the sum of very small values of δQ , corresponding to very small segments of the cyclic curve. The integral of a total differential over a closed contour is equal to zero:

$$\oint dU = U_1 - U_1 = 0. \quad (20.3)$$

This property of a total differential was described in detail in Sec. 15. With the help of (20.3), Eq. (20.2) can be reduced to the form

$$\oint \delta Q = \oint p dV = A.$$

(20.4)

This means that the total work performed during a cycle is due to the quantity of heat supplied to the system. For one part of the cycle, heat is supplied to the system, while for the other part, heat is taken away from the system. If a cycle is traversed in the clockwise direction, the heat supplied to the system is more than the heat taken away from it. Consequently, the system performs positive work.

If we go round the cycle in the counterclockwise direction, i.e. move from point 1 to point 2 along the curve L_2 and return along L_1 , the work will have the same absolute value but will be negative:

$$A_1 = \int_{L_2}^{(2)} p dV + \int_{L_1}^{(1)} p dV = - \left[\int_{L_1}^{(2)} p dV + \int_{L_2}^{(1)} p dV \right] = -A, \quad (20.5)$$

where A is the work (see (20.1)) done while going round the cycle in the clockwise direction. Thus, in this case the system itself does not perform work. Rather, work is performed on the system. The system transforms work into heat: heat is supplied to one part of the cycle and the system gives away more heat at another part than it receives. On completion of the cycle, the system returns to its initial state.

At each point of the cycle (Fig. 33), the temperature of the system is defined by the equation of state. Generally speaking, the temperature changes from point to point and is maintained at each point with the help of an appropriate thermostat. Hence, in order to complete a cycle we can assume that either the system is placed in a thermostat with varying temperature, or it moves from one thermostat to another at different temperatures. The second representation is often more visual, since in this case we can speak of a source and a sink which are assumed to exist permanently. In the first representation, we would have to speak of only one thermostat with a higher (lower) temperature.

It is difficult to determine at which points the system gives away heat to the thermostat and at which points receives heat from it. Theoretically, the answer to this question is quite simple: the system gives heat to the thermostat at points where $\delta Q < 0$ and receives heat at points where $\delta Q > 0$. In other words, the system releases heat if $dU + p dV < 0$ and receives heat if $dU + p dV > 0$. The points of transition from the segments where the system releases heat to the segments where it receives heat are determined by solving the equation $dU + p dV = 0$. The solution of this equation depends on the type of the cycle and the equation of state and is, generally speaking, not simple. Later we shall show how these points can be determined graphically.

EFFICIENCY. A system performing a cyclic process is essentially an engine which transforms the heat supplied to it by the thermostat into work (see (20.4)). The efficiency of the engine depends on the fraction of the supplied heat transformed by it into work, and is characterized by the quantity η defined as the ratio of the work A performed by



There is an infinitely large number of processes in which the heat supplied to a system is completely converted into work. Such processes, however, are not cyclic and will not be discussed here.

Since the total change in the entropy of a cycle is equal to zero, the entropy supplied to the system must be equal to the entropy given away by the system. This means that there can be no cycle in which heat is only supplied to the system and is delivered nowhere. Hence, the efficiency of the system is always less than unity.



Nicolas Léonard
Sadi Carnot
(1796-1832)

the engine during one cycle to the quantity of heat $Q^{(+)}$ supplied to it by the thermostats:

$$\eta = A/Q^{(+)} \quad (20.6)$$

The work A in this formula is graphically measured as the area of the closed curve representing the cycle, and is given by formula (20.4), and $Q^{(+)}$ is the amount of heat supplied by the thermostats to the system. This quantity is positive. Formula (20.4) can be rewritten as

$$\oint \delta Q = \int_{(+)} \delta Q + \int_{(-)} \delta Q = Q^{(+)} + Q^{(-)} = A, \quad (20.7)$$

where $\int_{(+)}$ and $\int_{(-)}$ are integrals over the segments of the cycle where heat flows into and out of the engine respectively, and $Q^{(-)}$ is the amount of heat leaving the engine (negative quantity). With the help of (20.7), expression (20.6) for the efficiency can be rewritten as

$$\eta = (Q^{(+)} + Q^{(-)})/Q^{(+)} = 1 + Q^{(-)}/Q^{(+)}. \quad (20.8)$$

This quantity is always less than unity, since $Q^{(-)}$ is negative.

CARNOT CYCLE. The Carnot cycle (Fig. 34) is the simplest in design but most important in principle. It consists of two isotherms connecting states 1, 2 and 3, 4 at temperatures T_1 and T_2 respectively, and two adiabats ($\delta Q=0$) connecting the states 2, 3 and 4, 1. The direction of the cycle is indicated by the arrows. Two thermostats are required for a Carnot cycle. The thermostat with the higher temperature T_1 is called the *source*, while the one with the lower temperature T_2 is called the *sink*. The system must be thermally insulated from the surroundings during the adiabatic parts of the cycle, i.e. the system must not exchange heat with the surroundings. Figure 35 shows the Carnot cycle in the S, T coordinates.

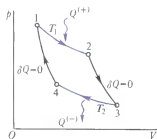


Fig. 34. Carnot cycle

The problem of mutual conversion of heat and work was first investigated in 1824 by the French engineer S. Carnot in his treatise "Réflexions sur la puissance motrice du feu et sur les machines propres à développer cette puissance". He obtained the results of fundamental importance which are at present associated with the cycle bearing his name. The concept of entropy did not exist at that time, and Carnot studied this problem from the point of view of thermogen. Nevertheless, the results obtained by Carnot are correct and retain their significance to this date.



Sir William Thomson
(Kelvin)
(1824-1907)

EFFICIENCY OF THE CARNOT CYCLE. In the case of an ideal gas, we can easily calculate $Q^{(+)}$ and $Q^{(-)}$. The amount of heat supplied to the system by the source on the isothermal segment 1, 2 is

$$Q^{(+)} = \int_{(1)}^{(2)} \delta Q = \int_{(1)}^{(2)} dU + \int_{(1)}^{(2)} p dV = RT_1 \ln(V_2/V_1), \quad (20.9)$$

since the change in the internal energy of an ideal gas in an isothermal process is equal to zero, while the second integral in this equation is given by (18.4). On the segment 3, 4, the system gives away heat to the sink at temperature T_2 . Similarly, we get

$$Q^{(-)} = \int_{(3)}^{(4)} \delta Q = RT_2 \ln(V_4/V_3). \quad (20.10)$$

It follows from Eq. (18.8) that

$$T_1 V_2^{-1} = T_2 V_3^{-1}, \quad T_1 V_1^{-1} = T_2 V_4^{-1}. \quad (20.11)$$

Dividing termwise the left- and right-hand sides of the first equation by the left- and right-hand sides of the second, we get

$$V_2/V_1 = V_3/V_4. \quad (20.12)$$

Consequently, we obtain

$$\ln(V_2/V_1) = -\ln(V_4/V_3). \quad (20.13)$$

Taking into account Eqs. (20.9), (20.10), and (20.13), we can rewrite Eq. (20.8) as follows:

$\eta = 1 - T_2/T_1.$

(20.14)

It should be noted that this formula is applicable to a reversible Carnot cycle.

CALCULATION OF EFFICIENCY WITH THE HELP OF ENTROPY. This calculation is made in the simplest way (Fig. 35). It follows from the definition of entropy that

$$\delta Q = T dS, \quad (20.15)$$

whence

$$Q^{(+)} = \int_{(1)}^{(2)} \delta Q = T_1 \int_{(1)}^{(2)} dS = T_1 (S_2 - S_1), \quad (20.16)$$

$$Q^{(-)} = \int_{(3)}^{(4)} \delta Q = T_2 \int_{(3)}^{(4)} dS = T_2 (S_4 - S_3).$$

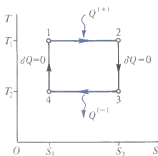


Fig. 35. Schematic diagram of the Carnot cycle in the T, S coordinates

Fig. 36. Schematic illustration of the second law of thermodynamics in the Kelvin formulation. The process shown in the figure is impossible

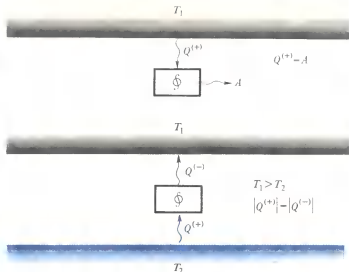


Fig. 37. Schematic illustration of the second law of thermodynamics in the Clausius formulation

Recalling that entropy does not change during an adiabatic reversible process (see (19.16)), we have $S_2 = S_3$ and $S_1 = S_4$, and hence formula (20.8) combined with (20.16) assumes the following form:

$$\eta = 1 + [T_2 (S_4 - S_3)] / [T_1 (S_2 - S_1)] = 1 - T_2 / T_1. \quad (20.17)$$

As expected, this formula coincides with (20.14).

KELVIN'S FORMULATION OF THE SECOND LAW OF THERMODYNAMICS. Formula (20.8) shows that the efficiency cannot exceed unity, but the possibility of the efficiency being equal to unity is not excluded by this formula. This may happen if $Q^{(-)} = 0$, i.e. if the heat supplied to the engine by the thermostat is completely transformed into work. The Kelvin principle states that there can be no cyclic process whose only result is the work and the heat exchange with only one heat reservoir (Fig. 36). The conversion of a certain amount of heat into work must be accompanied by a heat transfer from the heater to the refrigerator. This is one of the expressions of the second law of thermodynamics. It was put forward for the first time in 1851 by W. Thomson (Kelvin).

CLAUSIUS' FORMULATION. Another possible formulation of the second law of thermodynamics is that there is no cyclic process whose only result is the heat transfer from a colder to a hotter body. With such a formulation, the validity of the second law of thermodynamics is almost obvious: it is difficult to imagine a situation when no changes have occurred



The entire work performed in a cycle is due to the heat supplied to the system.

There can be no cyclic process whose only result is the work and heat exchange with only one heat reservoir (Kelvin's formulation of the second law of thermodynamics).

There can be no cyclic process whose only result is the heat transfer from a colder body to a hotter body (Clausius' formulation of the second law of thermodynamics).

$$\eta = 1 - \frac{T_2}{T_1}$$

but a certain amount of heat was transferred spontaneously from a colder body which became still cooler to a hotter body which became still hotter (Fig. 37).

This statement was proposed by Clausius in 1850 and refined by Kelvin in 1854. Kelvin, who independently formulated the second law of thermodynamics, subsequently remarked that his formulation differs only formally from that by Clausius.

EQUIVALENCE OF KELVIN'S AND CLAUSIUS' FORMULATIONS. If a process whose only result is the transfer of heat from a cooler body with temperature T_2 to a hotter body with temperature T_1 were possible,



we could take a heat engine with the source at the temperature T_1 and the sink at the temperature T_2 from which the heat is transferred to the source as a result of the above-mentioned process, i.e. this process as if cools the sink and heats the source:



This engine could take from the source the amount of heat $|Q_1|$ supplied to it as a result of the former process and transform a part of it into work. The final result would be that the state of the body at temperature T_2 does not change, and the entire heat taken from the body at the temperature T_1 is transformed into work:



Thus, the first of the above processes (if it were possible) creates a situation in which the second engine can do work without ultimately using the heat contained in the heater. Hence, the first two processes considered above jointly lead to the third process (Fig. 38). The left-hand side of the figure illustrates the Clausius formulation of the second law of thermodynamics, while the right-hand side, Kelvin's formulation. Thus, their equivalence has been proved.

REFRIGERATOR AND HEATER. If a cycle is traced in the reverse direction (see (20.5)), the engine does not produce any

Fig. 38. Schematic proof of the equivalence of the Kelvin and Clausius formulations of the second law of thermodynamics

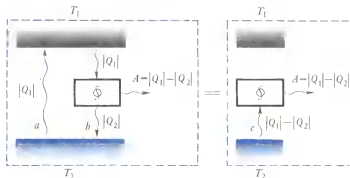
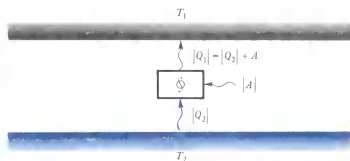


Fig. 39. Schematic diagram of a refrigerator



work. On the contrary, work is done on it. This work is converted into heat so that a certain amount of heat is taken from the colder body, the equivalent amount of heat due to work is added to it, and the total amount of heat is transferred to the source. Thus, the net result of the cycle is that the colder body from which heat is removed is cooled, while the hotter body which receives heat is heated. Such an engine operating on the basis of the reverse cycle is called a refrigerator or a heater depending on its purpose. The schematic diagram of a refrigerator is shown in Fig. 39. During the operation, the machine increases the temperature of a hotter body and decreases the temperature of a colder body. The efficiency of the device is characterized in two ways depending on its purpose.

If the efficiency is estimated by the ability of the device to increase the temperature T_1 of a hotter body, i.e. the machine operates as a heater, its efficiency is characterized by the coefficient

$$\xi_1 = \frac{|Q_1|}{|A|} = \frac{T_1}{T_1 - T_2} = \frac{1}{1 - (T_2/T_1)} = \frac{1}{\eta}, \quad (20.18)$$

which is equal to the ratio of the amount of heat transferred for heating to the work spent for this. On the other hand, if the efficiency of a device is estimated by the ability to decrease the temperature T_2 of a colder body, it is characterized by the coefficient

$$\xi_2 = \frac{|Q_2|}{|A|} = \frac{T_2}{T_1 - T_2} = \frac{1}{\eta} - 1. \quad (20.19)$$

In expressions (20.18) and (20.19) the quantities $|Q_1|$, $|Q_2|$, and $|A|$ are calculated with the help of the same formulas as used for calculating η in (20.14). The absolute values of the amount of heat and work are used instead of algebraic values (as in (20.8)) in order to make the representations in Fig. 39 and in Eqs. (20.18) and (20.19) more graphical.

OTHER POSSIBLE CYCLES. In principle, there is a very large number of possible cycles, since any closed curve on, say, p vs. V diagram has a cycle corresponding to it. Various cycles are used in engineering to convert heat into work or vice versa. Several dozens of cycles are used in practice. Their detailed account is given in engineering thermodynamics and appropriate branches of engineering.

Example 20.1. The temperature of 18°C must be maintained indoors, while outdoors the temperature is 35°C . It is known that heat in the room is generated by the equipment, bulbs, etc., people in the room and energy penetrating from outside. The thermal power generated in the room due to all these factors is equal to $P_T = 418$ W. Find the power of refrigerator which can ensure the required temperature, assuming that it operates at the maximum possible efficiency for refrigerators.

According to (20.19), the efficiency of a refrigerator is characterized by the coefficient

$$\xi_2 = T_2 / (T_1 - T_2) = 291/17 = 17.1.$$

Consequently, the power of the refrigerator can also be calculated by the same formula:

$$P = P_T / \xi_2 = 24.44 \text{ W}. \quad (20.20)$$

Example 20.2. The temperature of 35°C must be maintained indoors, while the temperature outdoors is 18°C . In spite of the fact that heat is evolved by devices and other heat sources in the room, the heat losses through the room walls are high. It is found that in order to maintain the constant temperature, heat must be supplied to the room at a power $P_T = 418$ W. Find the power of a heat pump

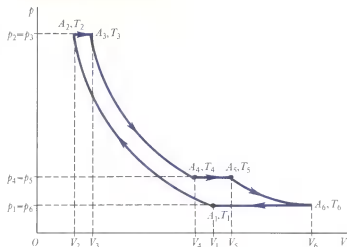


Fig. 40. An example of a cycle for which the efficiency maximization problem is solved

assuming that it operates at a maximum possible efficiency.

In accordance with (20.18), the efficiency of a heat pump is characterized by the coefficient

$$\xi_1 = 308/17 = 18.1.$$

Consequently, the same formula gives

$$P = P_T/\xi_1 = 23.09 \text{ W.} \quad (20.21)$$

Example 20.3. Consider the performance of the cycle consisting of three adiabats (A_1A_2 , A_3A_4 , and A_5A_6) and three isobars (A_2A_3 , A_4A_5 , and A_6A_1) (Fig. 40). Given the temperatures T_1 , $T_2 = \alpha T_1$, $T_3 = T_5 = \beta T_1$, $T_4 = \delta T_1$, and $T_6 = \varepsilon T_1$, where the parameters α , β , δ , and ε are determined by the operating conditions of the machine and its structural features. Find the relation between the parameters if the work done on the segment A_3A_4 is equal to the work done on A_5A_6 , and the work of the cycle as a function of the parameters and temperature T_1 (the number ν of moles of working gas and the molar heat capacity $C_p = \text{const}$ are given). Find the condition under which the work of the cycle is maximum for the given temperatures T_1 and T_3 and calculate the compression ratio p_2/p_1 . Find the efficiency of the cycle.

In accordance with (18.11), the condition that the works done on A_3A_4 and A_5A_6 are equal can be written in the form $\nu C_V(T_4 - T_3)/(\gamma - 1) = \nu C_V(T_6 - T_5)/(\gamma - 1)$. Hence, taking into account that $T_3 = T_5$, we get $T_4 = T_6$, i.e. $\delta = \varepsilon$.

For adiabats A_3A_4 and A_5A_6 , we obtain

$$\frac{T_3}{T_4} = \frac{\beta}{\delta} \left(\frac{p_3}{p_4} \right)^{(\gamma-1)/\gamma}, \quad \frac{T_5}{T_6} = \frac{\beta}{\varepsilon} \left(\frac{p_5}{p_6} \right)^{(\gamma-1)/\gamma} \quad (20.22)$$

If $\delta = \varepsilon$, then $p_3/p_4 = p_5/p_6$. Since $p_2 = p_3$, $p_4 = p_5$, and $p_6 = p_1$, we have $p_2/p_4 = p_4/p_1$.

For adiabat A_1A_2 , we get

$$T_2/T_1 = (p_2/p_1)^{(\gamma-1)/\gamma}. \quad (20.23)$$

But $T_2/T_1 = \alpha$, $p_2/p_1 = (p_2/p_4)(p_4/p_1) = (p_3/p_4)(p_5/p_6)$, and hence relation (20.23) can be written in the form

$$\alpha = (p_3/p_4)^{(\gamma-1)/\gamma} (p_5/p_6)^{(\gamma-1)/\gamma}. \quad (20.24)$$

Then, taking into account (20.22), we obtain $\alpha = (\beta/\delta)(\beta/\varepsilon) = \beta^2/\delta^2$ or

$$\delta = \beta/\sqrt{\alpha}. \quad (20.25)$$

The work of the cycle is equal to the energy supplied to the working body in the form of heat:

$$\begin{aligned} A = Q &= \nu C_p (T_3 - T_2) + \nu C_p (T_5 - T_4) + \nu C_p (T_1 - T_6) \\ &= \nu C_p T_1 (2\beta + 1 - \alpha - \delta - \varepsilon) \\ &= \nu C_p T_1 (2\beta + 1 - \alpha - 2\beta/\sqrt{\alpha}), \end{aligned} \quad (20.26)$$

where $\delta = \varepsilon = \beta/\sqrt{\alpha}$. In this relation $\beta = T_3/T_1 = \text{const}$, and hence the maximum can be found from the condition $dA/d\alpha = 0$ or $\nu C_p T_1 (\beta\alpha^{-3/2} - 1) = 0$, i.e. it can be attained at $\alpha = \beta^{2/3}$. The compression ratio can be determined from (20.23):

$$p_2/p_1 = \alpha^{\gamma/(\gamma-1)}. \quad (20.27)$$

The efficiency of the cycle is

$$\eta = A/Q^{(+)},$$

where A is defined by formula (20.26), and

$$Q^{(+)} = \nu C_p (T_3 - T_2) + \nu C_p (T_5 - T_4) = \nu C_p T_1 (2\beta - \alpha - \delta).$$

Consequently,

$$\eta = \frac{2\beta(1 - 1/\sqrt{\alpha}) + 1 - \alpha}{\beta(2 - 1/\sqrt{\alpha}) - \alpha}. \quad (20.28a)$$

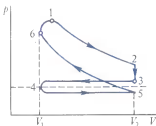


Fig. 41. A real cycle of a four-stroke combustion engine

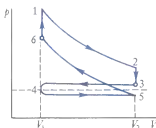


Fig. 42. An idealized cycle of a four-stroke combustion engine

The maximum efficiency is attained at $\alpha = \beta^{2/3}$ and is equal to

$$\eta_{\max} = (2\alpha^{3/2} - 3\alpha + 1) / [2(\alpha^{3/2} - \alpha)]. \quad (20.28b)$$

Substituting $\alpha = T_2/T_1$ or $\alpha = (p_2/p_1)^{(\gamma-1)/\gamma}$ into this formula, we can represent the efficiency of the cycle as a function of the compression ratio or of the ratio of temperatures corresponding to the beginning and the end of the compression stage. It can be seen that we must increase α in order to increase the efficiency.

Example 20.4. Find the efficiency of a four-stroke internal combustion engine. Assume that the mixtures of air with petrol vapour and air with combustion products behave as an ideal gas with the adiabatic exponent γ to a sufficiently high degree of accuracy. Figures 41 and 42 show the schematic diagrams of a real and an ideal cycle respectively.

In state 1, the chamber of volume V_1 contains the gas obtained after combustion of the compressed air-petrol mixture and having a high pressure p_1 . The working stroke (expansion of the gas along the adiabat 1, 2) is characterized by a positive work. In state 2 (lower dead point) the expansion reaches the maximum value, and the piston is in the extreme position. The volume V_2 is equal to the sum of the volumes of the combustion chamber and the cylinder. After the exhaust valve opens, the pressure in the cylinder drops to a value close to atmospheric pressure. In the ideal cycle these processes are considered to be instantaneous. In the real cycle, the exhaust valve opens before the piston reaches the lower dead point 2, and therefore the transition 2 $\rightarrow$ 3 is not strictly isobaric. On the segment 3 $\rightarrow$ 4 the exhaust gases remaining in the cylinder are swept out. At the upper dead point 4 the exhaust valve closes and the intake valve opens. The segment 4 $\rightarrow$ 5 corresponds to the fuel charging. At the point 5 the intake valve closes and on the segment 5 $\rightarrow$ 6 the working mixture is compressed. At the point 6 the mixture is fired, and the pressure in the compression chamber increases to p_1 . In the ideal cycle, it is assumed that the points 5 and 3 coincide, and hence the path 3 $\rightarrow$ 4 coincides with 4 $\rightarrow$ 5, and no work is done on the segment 3 $\rightarrow$ 4 $\rightarrow$ 5.

The work of the cycle is calculated by formula (18.10):

$$A = \frac{p_1 V_1}{\gamma - 1} \left[1 - \left(\frac{V_1}{V_2} \right)^\gamma \right] - \frac{p_6 V_1}{\gamma - 1} \left[1 - \left(\frac{V_1}{V_2} \right)^{\gamma-1} \right]$$

$$\begin{aligned}
 &= \frac{(p_1 - p_6) V_1}{\gamma - 1} \left[1 - \left(\frac{V_1}{V_2} \right)^{\gamma-1} \right] \\
 &= \frac{R (T_1 - T_6)}{\gamma - 1} \left[1 - \left(\frac{V_1}{V_2} \right)^{\gamma-1} \right], \quad (20.29)
 \end{aligned}$$

where T_1 and T_6 are the temperatures of states 1 and 6. In this formula, as usual, the work is calculated per mole of the substance. Considering that $\gamma - 1 = (C_p - C_v)/C_v = R/C_v$, formula (20.29) can be written in the form

$$A = C_v (T_1 - T_6) [1 - (V_1/V_2)^{\gamma-1}]. \quad (20.30)$$

The energy spent in increasing the temperature of a mole of the gas from T_6 to T_1 is equal to

$$Q^{(+)} = C_v (T_1 - T_6), \quad (20.31)$$

and hence the efficiency of the cycle is (see (20.6))

$$\eta = 1 - (V_1/V_2)^{\gamma-1}. \quad (20.32)$$

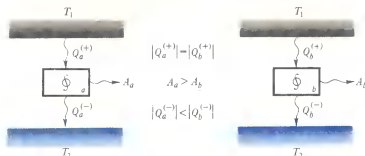
The ratio V_2/V_1 is called the compression ratio. The larger the compression ratio, the higher the efficiency. It turns out that the efficiency calculated from formula (20.32) is about twice as high as the efficiency of real internal combustion engines. The reason behind this discrepancy is that the operating conditions adopted for the ideal cycle considerably differ from operating conditions of a real cycle.

Sec. 21. ABSOLUTE THERMODYNAMIC TEMPERATURE SCALE

The absolute thermodynamic temperature scale is introduced proceeding from the fact that the efficiency of reversible engines based on the Carnot cycle is independent of the working substance. It is proved that the temperature introduced in this way is equivalent to that defined in Sec. 11. The meaning of the negative absolute thermodynamic temperature is discussed.

EFFICIENCY OF REVERSIBLE ENGINES BASED ON THE CARNOT CYCLE AND WITH IDENTICAL SOURCES AND SINKS. Reversible Carnot cycles with the same source and sink can be realized by using different engines having, for example, different working substances. It is stated that all reversible engines based on the Carnot cycle have the same efficiency. Before proving this statement, which is sometimes called Carnot's first theorem, it should be remarked that not all reversible engines have the same efficiency, but only those which are based on the Carnot cycle and have identical sources and sinks. For an arbitrary reversible cycle it is not enough to fix two temperatures and two thermostats, and this statement may not hold in the general case.

Fig. 43. Two engines a and b with different efficiencies: $\eta_a > \eta_b$



In other words, Carnot's first theorem can be formulated as follows: The efficiency of the Carnot cycle does not depend on the working substance and structural features of the device. For an engine with one source and one sink at constant temperatures, the Carnot cycle is the only possible working cycle, since if there are no other sources or sinks, the transition from the source temperature to the sink temperature and the reverse transition to complete the cycle can be made only adiabatically.

Let us prove this by contradiction. Suppose that (Fig. 43) the efficiency η_a of an engine



is higher than the efficiency η_b of another engine



We shall assume that $|Q_a^{(+)}| = |Q_b^{(+)}|$. Since $\eta_a > \eta_b$, $|Q_a^{(-)}| < |Q_b^{(-)}|$, i.e. the two engines receive equal amounts of heat from the source but must give off different amounts of heat to the sink: the engine with the higher efficiency must give off less heat to the sink than the other engine with the lower efficiency. We shall prove that this is impossible.

Let us start the engine a in the forward direction and use the work done by it to put into operation the engine b which works backwards, and hence operates as a refrigerator:



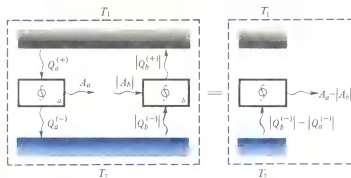


Fig. 44. To the proof of the identity of efficiencies of reversible engines having the same sinks and sources

Then the engine b will take from the sink an amount of heat $|Q_b^{(-)}|$ which is modulo larger than the amount of heat $|Q_a^{(-)}|$ given off to the sink by the first engine. Thus, the sink loses a certain amount of heat equal to the difference between the amounts of heat indicated above. On the other hand, the source will receive from the second engine the same amount of heat $|Q_b^{(+)}|$ as was taken from it by the first engine, since $|Q_a^{(+)}| = |Q_b^{(+)}|$. The net result is the extraction of heat from the sink and complete conversion of it into work (see Fig. 44), which is in contradiction to the second law of thermodynamics in Kelvin's formulation. Thus, we have proved that two reversible heat engines based on the Carnot cycle with the same sources and sinks cannot have different efficiencies.

On the basis of formula (20.14) we can now state that the efficiency of a reversible Carnot cycle does not depend on the working substance and structural features of the engine and is determined only by the ratio of temperatures of the source and the sink. The efficiency is always lower than unity and approaches it when either the temperature of the sink tends to zero or the temperature of the source tends to infinity.

ABSOLUTE THERMODYNAMIC TEMPERATURE SCALE. It has been proved above that the efficiency

$$\eta = (Q^{(+)} + Q^{(-)})/Q^{(+)} = 1 + Q^{(-)}/Q^{(+)} \quad (21.1)$$

has the same value for all reversible engines operating with a source at temperature T_1 and a sink at temperature T_2 . Hence, the ratio $Q^{(-)}/Q^{(+)}$ is a function of only T_1 and T_2 : $(Q^{(-)}/Q^{(+)}) = f(T_2, T_1)$.

Suppose that we have a body with a temperature T_3 in the interval between T_1 and T_2 . This body may serve as

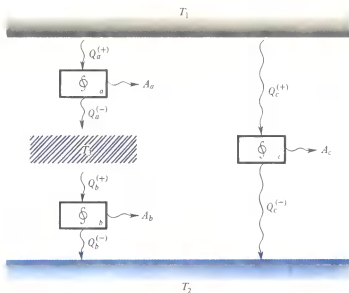


Fig. 45. To the definition of the absolute thermodynamic temperature scale

a source as compared to the temperature T_2 and as a sink in comparison with T_1 . Let us use it as shown in Fig. 45. The engines a , b , and c are reversible, and in accordance with what has been proved above, have identical efficiencies.

The combination of two reversible engines a and b is a reversible engine whose efficiency must be equal to the efficiency of the engine c . This means that

$$Q_a^{(+)} = Q_c^{(+)}, \quad Q_b^{(-)} = Q_c^{(-)}, \quad Q_a^{(-)} = -Q_b^{(+)}, \quad A_a + A_b = A_c. \quad (21.3)$$

Relation (21.2) for these engines has the form

$$\begin{aligned} Q_c^{(-)}/Q_c^{(+)} &= f(T_2, T_1), \quad Q_a^{(-)}/Q_a^{(+)} = f(T_3, T_1), \\ Q_b^{(-)}/Q_b^{(+)} &= f(T_2, T_3). \end{aligned} \quad (21.4)$$

Taking into account (21.3), we get

$$\begin{aligned} f(T_2, T_1) &= Q_c^{(-)}/Q_c^{(+)} = Q_b^{(-)}/Q_a^{(+)} = -(Q_b^{(-)}/Q_b^{(+)}) (Q_a^{(-)}/Q_a^{(+)}) \\ &= -f(T_2, T_3) f(T_3, T_1). \end{aligned} \quad (21.5)$$

The left-hand side of this equation does not depend on T_3 . Hence the function must be such that the temperature T_3 in the product of two such functions in (21.5) is cancelled out.

This means that

$$f(T_2, T_1) = -\varphi(T_2)/\varphi(T_1), \quad (21.6)$$

where φ is a new function. Thus we have proved that the ratio of amounts of heat in the Carnot cycle can be expressed as

$$Q^{(-)}/Q^{(+)} = -\varphi(T_2)/\varphi(T_1). \quad (21.7)$$

The function φ can in principle be chosen in thousands of ways and thus we will obtain thousands of temperature scales. Kelvin proposed the simplest dependence

$$\varphi(T_2)/\varphi(T_1) = T_2/T_1, \quad Q^{(-)}/Q^{(+)} = -T_2/T_1, \quad (21.8)$$

which defines the absolute thermodynamic temperature scale. In this scale, the efficiency (21.1) of a reversible engine based on the Carnot cycle is

$$\eta = 1 - T_2/T_1, \quad (21.9)$$

which coincides with (20.14) corresponding to the same cycle, but where T_2 and T_1 indicate the temperature measures with the help of an ideal gas thermometer (see Sec. 11). Consequently, the fact that Eqs. (21.9) and (20.14) coincide proves the identity of these temperatures. In other words, the temperature scale established in Sec. 11 is indeed the absolute thermodynamic scale. On the other hand, it was shown that the temperature T determined by an ideal gas thermometer is equivalent to that introduced in (8.15) as a formal parameter used in the analysis of the Gibbs distribution. Consequently, in the above presentation the letter T denoted temperature everywhere on the same temperature scale and was the absolute thermodynamic temperature.

NEGATIVE ABSOLUTE THERMODYNAMIC TEMPERATURE. Proceeding from the second law of thermodynamics, we can prove that negative thermodynamic temperatures are impossible.

Suppose that a body having a negative temperature T_2 is chosen as a sink in the Carnot cycle. The right-hand side of Eq. (21.8) is positive as well as $Q^{(+)}$, viz. the amount of heat taken from the source. Consequently, $Q^{(-)}$ is also a positive quantity. This means that such an engine must also receive heat from the sink, i.e. the heat is taken from the source and from the sink and is entirely converted into work. But this is

in contradiction to the second law of thermodynamics in Kelvin's formulation, and hence such a situation cannot be realized. Thus, negative temperature is impossible.

And still the concept of "negative thermodynamic temperature" is used in certain physical situations. For example, in Perrin's experiments on verification of the Boltzmann distribution (see Sec. 9) a thorough stirring of the liquid containing suspended particles can be used to make the density of particles the same at all altitudes. Since this state is essentially a nonequilibrium state, it cannot be described with the help of the Boltzmann distribution (9.26). However, we can formally assume that this state can also be described in terms of the Boltzmann distribution. Since in this case $n_0(h)$ must be equal to $n_0(0)$ in formula (9.26), it can be said that the temperature of the system is $T = \pm \infty$. This does not lead to any misunderstanding if we know what we are talking about. On the other hand, this concept can be used to characterize a specific physical situation in a concise and convenient form. In this case, the Boltzmann formula (9.26) plays the role of an interpolation formula in which the parameter T assumes a negative value. Suppose that the concentration of particles in Perrin's experiment grows with height. Obviously, this can be attained with the help of some external effect (if, for example, particles having different velocities are introduced into the liquid at different altitudes). The indication of a negative value of T can then signify an increase in the particle density with height. This situation could be described with the help of tables or a certain empirical formula for each specific case. The concept of negative temperature makes it possible to avoid all these procedures and describe some physical situations with a sufficiently high degree of accuracy.

The impossibility of negative thermodynamic temperatures was strictly proven in the analysis of quasistationary reversible processes. This proof, however, does not imply that the parameter $\beta = 1/(kT)$ can never be ascribed a negative value. The impossibility of negative values of β for an equilibrium state of ordinary systems follows from the fact that the energy of such systems is bounded from below and not from above. The partition function (7.16) which characterizes all the properties of a system in an equilibrium state must be finite, which is possible only for $\beta > 0$. If, however, a system is such that the partition function corresponding to it has a finite value for negative β 's as well, it can be said that the system is in an equilibrium state at a negative temperature and associate this statement not only with purely terminological considerations as in examples with Perrin's



Negative thermodynamic temperatures are impossible, but the concept of negative temperature can be used for the analysis of certain physical situations.

All reversible engines working on Carnot's cycle have the same efficiency which is independent of the nature of the working substance (Carnot's first theorem).

experiments. This immediately leads to the conclusion that the system must have only energies from a finite interval, i.e. must be bounded from above and from below with respect to energy. In this case, the partition function has a finite value, and the system has quite definite functions of state at $\beta < 0$. The behaviour of the system upon variation of the parameter β can be investigated quantitatively, i.e. we can operate with it as with the system in an equilibrium state. In this case, the negative temperature assumes a physical meaning in a certain sense.

However, unlike ordinary systems for which negative temperatures are impossible, these systems, firstly, cannot exist in an equilibrium state for an infinitely long time, and secondly, they cannot be transferred to a state with a negative temperature with the help of reversible quasi-stationary processes. Such a transition is realized as a result of a strong nonstationary effect on the system.

Let us consider a system of particles with spin $1/2$ and the corresponding magnetic moment p_m . In an external magnetic field B , the magnetic moment of such a particle can be oriented either along the field or against the field, and the energy of interaction may assume accordingly the values $\varepsilon_0 = \varepsilon_{\min} = -p_m B$ and $\varepsilon_1 = \varepsilon_{\max} = p_m B$, while the energy of the system of n particles lies between $E_{\min} = -p_m n B$ and $E_{\max} = p_m n B$. Thus, the conditions under which the partition function must be finite are satisfied. However, in order to impart a real meaning to the analysis of the system, we must assume that the interaction between the spins and the medium (e.g. crystal lattice) is sufficiently weak. In this case, we can isolate the degrees of freedom associated with spin from other degrees of freedom and take them into account only in the partition function, if other degrees of freedom were absent. If the interaction with the medium is not neglected, we must take into account all the degrees of freedom, and the partition function will contain all the values of energy allowed for the particles. These values are not bounded from above, and negative values of β will become impossible if the partition function is finite. If we disregard the interaction of the system with the medium, the system can be treated as an equilibrium system with negative temperature only during short intervals of time.

If we assume that interaction between spins is weak, the partition function of the system, calculated by the same method as in (12.24b), is equal to $Z = Z_1^n$, where

$$Z_1 = e^{p_m \beta B} + e^{-p_m \beta B} = 2 \cosh(p_m \beta B). \quad (21.10)$$

Thus, the partition function, and hence all thermodynamic equilibrium characteristics of the system, are defined both for positive and negative values of β . When β is negative, we can say that the system is at a negative absolute temperature. The parameter β varies continuously from $-\infty$ to ∞ , the partition function varying continuously with it. However, the temperature $T = 1/(k\beta)$ undergoes a discontinuity at $\beta = 0$, namely, $T(\beta \rightarrow -0) \rightarrow -\infty$, while $T(\beta \rightarrow +0) \rightarrow \infty$. Therefore, the temperatures $T = \infty$ and $T = -\infty$ correspond to the same physical state, and the transition from states with positive temperatures to those with negative temperatures is realized through $T = \infty$ rather than through $T = 0$ K.

Let us trace the change in the distribution of magnetic orientations with temperature in a given field. We shall follow the variation of the partition function Z (whose value is completely determined by Z_1) and the number of particles which is fixed. Considering that the energy of an atom having the magnetic moment $\mathbf{p}_m$ in the field $\mathbf{B}$ is $-(\mathbf{p}_m \cdot \mathbf{B})$, we see that the first term of Z_1 in (21.10) describes the orientation of magnetic moments along the field, and the second term, against the field. At very low positive temperatures $T \rightarrow +0$ K the first term is rather large, while the second is very small. This means that at a positive temperature close to 0 K, all the magnetic moments are oriented along the field, and all the particles are on the lower energy level, the upper level being unoccupied. As the positive temperature T increases, the parameter β remains positive and decreases. Hence the first term in Z_1 decreases and the second increases. This means that the number of particles whose magnetic moments are oriented along the field decreases, while the number of particles with the opposite orientation increases. From the point of view of energy this means that the population density of the lower level decreases and of the upper, increases. For $T \rightarrow +\infty$, $\beta \rightarrow +0$, and the population densities of the levels become equal. In this case, there is no preferable orientation of magnetic moments. The number of particles with magnetic moments along the field is equal to the number with moments against the field.

As β goes over through 0 to negative values, Z_1 continuously changes, which causes a continuous change in the distribution of particles among energy levels. At small negative values of β , the first term in Z_1 becomes somewhat less than the second term. This means that the system becomes ordered, but the orientation of magnetic moments against the field $\mathbf{B}$ predominates. In other words, the population density of the upper energy level becomes higher than that of the lower level. In this case, the temperature is

negative and high in the absolute value. With a further decrease of β towards negative values, the role of the second term in Z_1 becomes more significant. The negative temperature in this process increases and approaches the value zero from negative values. Thus, as the negative temperature increases, the magnetic moments get oriented against the field, the population density of the upper energy level increases and of the lower level decreases. As $T \rightarrow -0$ K all the magnetic moments are directed against the field and all the particles populate the upper level. The lower energy level is unoccupied. This state corresponds to the complete population inversion of energy levels. Thus, the negative thermodynamic temperatures are characterized by an inverse population density of energy levels. The inversion is the stronger the closer the negative temperatures to 0 K.

The total energy of a system at a negative temperature is higher than at a positive temperature. Consequently, in order to make a transition from a state at a positive temperature to a state at a negative temperature, energy must be supplied to the system rather than taken away from it.

In spin systems, negative temperatures can be created by a rapid change in the magnetic field in which the magnetic moments have been predominantly oriented along the field at a positive temperature. If at a rapid change in the direction of the magnetic field the magnetic moments do not have time to "catch up" with it, a negative temperature will exist for a certain time in the spin system. The levelling out of the inverse population corresponds to the tendency of T to $-\infty$. At $T = -\infty$, the population densities level out, and there is no population inversion at positive T 's. Spin systems with negative temperatures were observed in crystals, and their behaviour was in accord with general regularities discussed above. The inverse population of energy levels forms the basis for the operation of optical amplifiers and oscillators (lasers).

Sec. 22. THE SECOND LAW OF THERMODYNAMICS

The definition of entropy given in Sec. 19 for an ideal gas is generalized for an arbitrary case. The second law of thermodynamics is formulated in terms of entropy, and its statistical nature is analyzed.

CARNOT'S SECOND THEOREM. Let us prove that the efficiency of an irreversible engine based on the Carnot cycle is always lower than the efficiency of a reversible engine operating with the same cycle and having the same source and sink. The proof is obtained by contradiction in the same way as was used in Sec. 21 in the analysis of the efficiency of reversible engines having the same sources and sinks. Suppose that the efficiency of an irreversible engine is higher

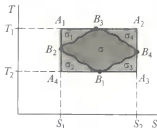


Fig. 46. To the proof of the theorem on the maximum efficiency of a reversible Carnot cycle

than the efficiency of a reversible one. We shall start the irreversible engine in the forward direction (machine *a* in Fig. 44), and the reversible engine (machine *b*) in backward direction. Repeating the considerations of Sec. 21, we arrive at the conclusion that this is impossible. Thus we have proved that the efficiency of the irreversible engine based on the Carnot cycle cannot be higher than the efficiency of the reversible engine with the same source and sink. It should be emphasized that we are comparing the efficiencies of reversible and irreversible engines based on the same Carnot cycle and not the engines operating with different cycles. We can find an arbitrary number of reversible engines operating on the basis of some cycle and having higher efficiency than that of a reversible engine operating on some other cycle.

Let us now prove that the efficiency of a reversible Carnot cycle is always higher than the efficiency of any other reversible cycle whose maximum and minimum temperatures are respectively equal to the temperatures of the source and the sink of the Carnot cycle. In the proof we shall use the cycle shown in Fig. 46 on the T, S plane. The reversible cycle different from the Carnot cycle and satisfying the conditions of the theorem is depicted by a closed curve inside the rectangle $A_1A_2A_3A_4$ formed by tangents A_1A_2 and A_3A_4 to it. Integrating the relation $\delta Q = T dS = dU + dA$ over the cycle, we obtain

$$\oint \delta Q = \oint T dS = \oint dU + \oint dA = A,$$

since $\oint dU = 0$. In the given case, for the Carnot cycle we have

$$\begin{aligned} A_C &= \oint T dS = T_1 \int_{A_1}^{A_2} dS + T_2 \int_{A_3}^{A_4} dS \\ &= T_1 (S_2 - S_1) + T_2 (S_1 - S_2) = (T_1 - T_2) (S_2 - S_1). \end{aligned}$$

The amount of heat supplied to the cycle is

$$Q_C^{(+)} = \int_{A_1}^{A_2} T dS = T_1 \int_{A_1}^{A_2} dS = T_1 (S_2 - S_1),$$

and hence the efficiency of this cycle is

$$\eta_C = \frac{A_C}{Q_C^{(+)}} = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1},$$

which is identical to the expression obtained earlier.

For the other engine whose cycle is depicted by the curve

inside the rectangle corresponding to the Carnot cycle we get

$$\begin{aligned} A &= \oint T dS = \sigma = (T_1 - T_2)(S_1 - S_2) - \sigma_1 - \sigma_2 - \sigma_3 - \sigma_4 \\ &= A_C - \Delta_{1234}, \quad \Delta_{1234} = \sigma_1 + \sigma_2 + \sigma_3 + \sigma_4. \end{aligned}$$

The amount of heat supplied to this engine is

$$\begin{aligned} Q^{(+)} &= \int T dS = T_1(S_2 - S_1) - \sigma_1 - \sigma_4 = Q_C^{(+)} - \Delta_{14}, \\ \Delta_{14} &= \sigma_1 + \sigma_4, \end{aligned}$$

whence

$$\eta = \frac{A}{Q^{(+)}} = \frac{A_C - \Delta_{1234}}{Q_C^{(+)} - \Delta_{14}}.$$

Considering that $A_C = \eta_C Q_C^{(+)}$, we can transform this expression as follows:

$$\begin{aligned} \eta &= \frac{\eta_C Q_C^{(+)} - \Delta_{14} - \Delta_{23}}{Q_C^{(+)} - \Delta_{14}} \\ &= \frac{\eta_C (Q_C^{(+)} - \Delta_{14}) + \eta_C \Delta_{14} - \Delta_{14} - \Delta_{23}}{Q_C^{(+)} - \Delta_{14}} \\ &= \eta_C - \Delta_{14} (1 - \eta_C) / (Q_C^{(+)} - \Delta_{14}) - \Delta_{23} / (Q_C^{(+)} - \Delta_{14}), \end{aligned}$$

$$\Delta_{23} = \sigma_2 + \sigma_3,$$

whence it follows that $\eta \leq \eta_C$.

The equality $\eta = \eta_C$ can be attained only when $\Delta_{14} = 0$ and $\Delta_{23} = 0$, i.e. when the other cycle under consideration is also a Carnot cycle. This proves the theorem. If the curve depicting the other cycle is not in contact with the vertical segments of the Carnot cycle in Fig. 46 but either crosses them or lies inside the rectangle, the proof is similar and the result is the same. We leave it to the reader to independently derive it.

Returning to Carnot's second theorem, let us write it analytically. The efficiency of a machine is always given in the form (21.1), while for a reversible cycle with the same source and sink it is given in the form (21.9). For the case considered above, the theorem we have proved can be written analytically as follows:

$$1 + Q^{(-)}/Q^{(+)} \leq 1 - T_2/T_1 \quad (22.1)$$

or, alternatively,

$$Q^{(-)}/Q^{(+)} \leq -T_2/T_1. \quad (22.2)$$

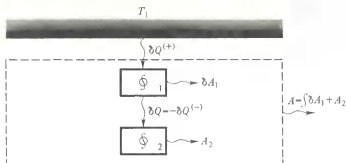


Fig. 47. To the proof of the Clausius inequality for an arbitrary cycle

The minus sign in this inequality indicates that $Q^{(+)}$ and $Q^{(-)}$ have different signs. Relation (22.2) written in the form

$$Q^{(+)} / T_1 + Q^{(-)} / T_2 \leq 0, \quad (22.3)$$

is called the **Clausius inequality** for the Carnot cycle. Obviously, it becomes an equality for a reversible cycle. Let us generalize this inequality to an arbitrary cycle and show that it becomes an equality only for reversible cycles.

CLAUSIUS INEQUALITY. We shall consider an engine for obtaining work, shown schematically in Fig. 47. The reservoir is at a constant temperature T_1 . The heat $\delta Q^{(+)}$ taken from it is transferred to the reversible engine 1 operating periodically on the basis of the Carnot cycle. During a cycle, the engine performs work δA_1 and transfers the amount of heat δQ at a temperature T to the cyclic engine 2 which can be an arbitrary machine performing any cycle, reversible or not. Generally speaking, the temperature T is not constant and depends on the processes occurring in engine 2 and in surrounding medium. Engine 2 performs the work A_2 during a cycle. Suppose that the duration of cycles of engine 1 is much (infinite number of times) shorter than the cycle duration of engine 2. Therefore, we can assume that the temperature T is constant during a cycle of engine 1.

The work δA_1 performed by reversible engine 1 during a cycle is

$$\begin{aligned} \delta A_1 &= \delta Q^{(+)} \left(1 - \frac{T}{T_1} \right) = \delta Q^{(+)} \frac{T}{T_1} \left(\frac{T_1}{T} - 1 \right) \\ &= -\delta Q^{(-)} \left(\frac{T_1}{T} - 1 \right) = \delta Q \left(\frac{T_1}{T} - 1 \right), \end{aligned} \quad (22.4)$$

$$\frac{Q^{(+)}}{T_1} + \frac{Q^{(-)}}{T_2} \leq 0$$

where we took into account formula (22.2) which in the case of the reversible engine 1 becomes an equality, and δQ is the amount of heat which must be positive if it is supplied to engine 2.

The work A_2 performed by engine 2 during a cycle is given in accordance with the general formula (20.4) by

$$A_2 = \oint \delta Q. \quad (22.5)$$

The total work produced by the two engines during a cycle of engine 2 is

$$A = \oint \delta A_1 + A_2 = \oint (\delta A_1 + \delta Q) = T_1 \oint \frac{\delta Q}{T}. \quad (22.6)$$

Let us consider these equalities in greater detail. The integral $\oint \delta A_1$ is taken over many cycles of engine 1 whose total duration is equal to the duration of a cycle of engine 2. The integral $\oint (\delta A_1 + \delta Q)$ is taken over a cycle of engine 2 (δA_1 is expressed in terms of δQ via formula (22.4)).

In accordance with the Kelvin principle, a system consisting of two engines cannot have work as the only result of its cycle. In the scheme under consideration, heat does not leave the system (the dashed line envelopes the two engines as well as all other things connected with their operation, i.e. no heat can leave the system by definition). Hence, this system can operate only if work is done on it, or at least if the work produced by it is equal to zero:

$$A \leq 0.$$

Taking into account (22.6), we can write this inequality as

$$\oint \frac{\delta Q}{T} \leq 0, \quad (22.7)$$

since $T_1 = \text{const} > 0$. It holds for any cycle performed by engine 2. This expression is called the **Clausius inequality** and is valid for any cycle.

Let us prove that expression (22.7) becomes a strict equality for a reversible engine. Suppose that engine 2 is reversible but expression (22.7) is a strict inequality, i.e.

$$A < 0. \quad (22.8)$$

However, if engine 2 is reversible, the entire system is reversible since engine 1 is reversible by definition. Hence we can start the system in the backward direction, and then $A >$

$$\oint \frac{\delta Q}{T} = 0$$



Rudolf Julius Emanuel
Clausius
(1822-1888)



A reversible engine based on the Carnot cycle has the maximum efficiency not only because it is reversible but also because heat is supplied to it only at maximum temperature and is removed only at minimum temperature.

The entropy of an isolated system increases ultimately due to equal probability of all its microscopic states through which the system attains the most probable macroscopic state.

> 0 , which is in contradiction with the Kelvin principle. Consequently, condition (22.8) does not hold, and the only possible sign is equality. Thus, the equality sign in the Clausius inequality (22.7) corresponds to reversible processes, while the inequality corresponds to irreversible ones.

Relation (22.7) for reversible processes (with the equality sign) was obtained in 1854 by Clausius and independently by Thomson. For irreversible processes, inequality (22.7) was substantiated by Clausius in 1862-1865. He introduced the concept of entropy as a measure of the ability of heat to be converted into other forms of energy.

ENTROPY. For reversible processes, inequality (22.7) becomes an equality:

$$\oint \frac{\delta Q}{T} = 0. \quad (22.9)$$

This means that the integrand in (22.9) is a total differential:

$$\delta Q/T = dS, \quad (22.10)$$

where S is the entropy. Thus, formula (19.3) for the entropy of an ideal gas is generalized for an arbitrary system. The analysis of the physical meaning of entropy (see Sec. 19) remains valid. In particular, the Boltzmann formula (19.12) is valid for all cases and not only for an ideal gas.

THE SECOND LAW OF THERMODYNAMICS. Suppose that a closed system, i.e. the system isolated from other systems, goes over from state 1 to state 2 as a result of some process (Fig. 48). Let us return the system to state 1 with the help of a reversible process. Of course, in this case the system is no longer isolated. By returning the system to state 1, we complete the cycle to which the Clausius inequality (22.7) can be applied:

$$\oint \frac{\delta Q}{T} = \int_{L_1}^{(2)} \frac{\delta Q}{T} + \int_{L_2}^{(1)} \frac{\delta Q}{T} \leq 0. \quad (22.11)$$

During the transition $1 \rightarrow 2$ along L_1 the system was isolated, and hence δQ in the integral over L_1 must be equal to zero, and the integral vanishes. On the other hand, according to (22.10) we can assume that the integrand in the last integral of (22.11) is $(\delta Q/T) = dS$, since the transition $2 \rightarrow 1$ is reversible. Thus, expression (22.11) becomes

$$\int_{L_2}^{(1)} \delta Q/T = \int_{(2)}^{(1)} dS = S_1 - S_2 \leq 0,$$

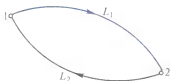


Fig. 48. To the proof of the nondecrease of the entropy in closed systems

or

$$S_2 \geq S_1.$$

(22.12)

This means that as the closed system goes over from state 1 with entropy S_1 to state 2 with entropy S_2 , its entropy either increases or remains unchanged. This is just the expression for the second law of thermodynamics. In a simpler form, the second law of thermodynamics can be formulated as follows: the entropy of an isolated system does not decrease during the processes. It is significant that this statement deals with isolated systems. Depending on the nature of processes, the entropy of nonisolated systems may increase, decrease, or remain unchanged as can be seen from the example of an ideal gas. It should be noted that the entropy of an isolated system remains unchanged only in reversible processes. In irreversible processes, it increases. Since, as a rule, the processes in an isolated (closed) system proceed, irreversibly, the entropy of an isolated system practically always increases. The increase in entropy indicates that the system approaches the state of thermodynamic equilibrium.

Thus, the first law of thermodynamics describes the quantitative relations between the quantities characterizing a system while the state of the system changes but gives no idea about the direction of these changes. The second law indicates the direction of changes in the system if they must occur or the absence of the changes if they cannot take place.

STATISTICAL NATURE OF THE SECOND LAW OF THERMODYNAMICS. Entropy is equal to the logarithm of the number of microscopic states, through which a given macroscopic state is realized, multiplied by the Boltzmann constant (see (19.12)). An increase in the entropy of an isolated system means that the system changes in the direction of the most probable, i.e. equilibrium, state. During this change, however, fluctuations are possible in principle, and during a certain interval of time the system changes towards less probable macroscopic states. During this interval, the entropy of the isolated system decreases rather than increases or remains unchanged. Hence, the law of nondecreasing entropy in an isolated system does not absolutely prohibit a decrease in entropy. The relative role of fluctuations increases for small systems (see Sec. 6). Consequently, the probability that the prohibition of decreasing entropy is violated is considerably higher for systems containing a relatively small number of particles.

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No irreversible engine can be more efficient than a reversible engine which is based on the Carnot cycle and has the same source and sink as the irreversible engine (the second Carnot theorem).

In processes occurring in an isolated system the entropy increases. In nonisolated systems, the entropy may increase, decrease, or remain unchanged depending on the nature of the process occurring in it.

However, the law of nondecreasing entropy in isolated systems containing not very small number of particles is practically absolute. Its violation is as unlikely as, for example, the event that the air contained in a room will suddenly squeeze into a glass which stands on the table.

THE CHANGE IN ENTROPY IN IRREVERSIBLE PROCESSES. The calculation is based on the fact that the entropy is a function of state. If a system has accomplished a transition from one state to another as a result of an irreversible process, it is logical to mentally transfer the system from the first state to the second with the help of some reversible process and calculate the entropy change in this case. It will be equal to the entropy change during the irreversible process.

Let us consider the change in entropy when the temperatures of two bodies brought into thermal contact equalize. We shall denote the masses, specific heats at constant volume, and temperatures of the first and the second body by m_1 , c_{V1} , T_1 and m_2 , c_{V2} , T_2 respectively. In order to simplify calculations, we shall assume that heat exchange occurs at a constant volume ($V_{1,2} = \text{const}$) of each of the bodies, specific heats c_{V1} and c_{V2} do not depend on temperature, and $T_1 > T_2$. We can find the temperature T_3 of the bodies after the attainment of thermodynamic equilibrium from the equation

$$m_1 c_{V1} (T_1 - T_3) = m_2 c_{V2} (T_3 - T_2),$$

which yields

$$T_3 = \frac{m_1 c_{V1} T_1 + m_2 c_{V2} T_2}{m_1 c_{V1} + m_2 c_{V2}}. \quad (22.13)$$

The transition from state 1 to state 2 is shown schematically in Fig. 49. The irreversible process of heat exchange when two bodies are brought in contact is depicted in Fig. 49a. In the initial state, the bodies m_1 and m_2 are isolated from one another and have different temperatures. Then they are brought into thermal contact. As a result of heat exchange, the bodies go over to state 2. However, a transition from state 1 to 2 can also be accomplished with the help of reversible processes (Fig. 49b). In this case, the bodies m_1 and m_2 are considered to be isolated, and each of them is brought to state 2 at the same temperature T_3 . After this they are brought in contact, but this does not introduce any change into their state. Hence the initial and final states are the same in both cases, and the change in entropy can be

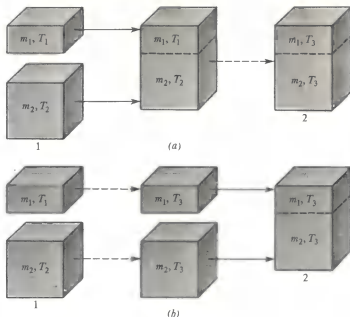


Fig. 49. The method of calculation of the change in entropy during the thermal contact of bodies

calculated by using formula (22.10) for a reversible process:

$$\Delta S = \int_{(1)}^{(2)} \frac{\delta Q}{T} = m_1 c_{V1} \int_{T_1}^{T_3} \frac{dT}{T} + m_2 c_{V2} \int_{T_2}^{T_3} \frac{dT}{T}, \quad (22.14)$$

where $\delta Q = mc_V dT$. After evaluating the integrals, we obtain

$$\Delta S = m_1 c_{V1} \ln (T_3/T_1) + m_2 c_{V2} \ln (T_3/T_2). \quad (22.15)$$

This is just the entropy change in irreversible process. By a direct substitution of (22.13) into (22.15), we find that $\Delta S > 0$. It is, however, clear without calculations that this should be so according to the second law of thermodynamics in the form (22.12). We can make sure of it in a different way too. Let us realize the heat exchange between two bodies with the help of a certain engine which reversibly transfers heat from the hotter body to the colder one. Let, for the sake of definiteness, T_1 be higher than T_2 . Then the amount of heat $|\delta Q|$ taken from the hotter body will change its entropy by $\Delta S_1 = -|\delta Q|/T_1$, while the same amount of heat transferred to the colder body will increase its entropy by $\Delta S_2 = |\delta Q|/T_2$. Consequently, the total change in entropy of the two bodies in thermal contact upon a transfer of $|\delta Q|$ from the hotter body to the colder body is equal to $\Delta S =$

2. Thermodynamic Method

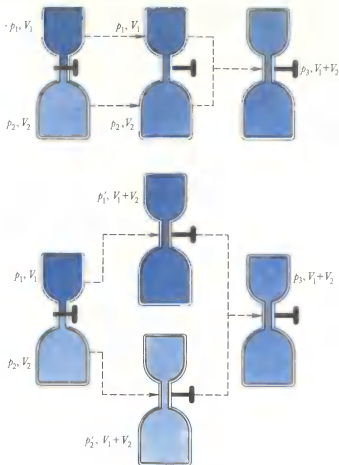


Fig. 50. The method of calculation of the change in entropy during the pressure equalization in a gas

$= \Delta S_1 + \Delta S_2 = |\delta Q| \left[(1/T_2) - (1/T_1) \right] > 0$, since $T_1 > T_2$, i.e. the entropy actually increases during heat exchange.

By way of another example, let us consider the pressure equalization in a gas whose two parts were under different pressures before the contact, but had the same temperature T . The system is assumed to be thermally insulated, and the density of the gas is so low that it can be considered ideal. This means that the internal energy depends only on temperature and does not change upon mixing. In this case, an equilibrium process which replaces the nonequilibrium process consists in isothermal expansion of both parts of the gas having volume V_1 and V_2 to the total volume $V_1 + V_2$ (Fig. 50). Then

$$\Delta S = \int_{(1)}^{(2)} dS = \int_{V_1}^{V_1+V_2} \frac{p dV}{T} + \int_{V_2}^{V_1+V_2} \frac{p dV}{T},$$

because $T dS = dU + p dV = p dV$ ($dU = 0$).

Considering that $p/T = mR/(MV)$, where M is the molar mass of the gas, we obtain after integration

$$\Delta S = \frac{m_1}{M} R \ln \frac{V_1 + V_2}{V_1} + \frac{m_2}{M} R \ln \frac{V_1 + V_2}{V_2}.$$

The pressure of the gas mixture is found from the Dalton law:

$$p_3 = (p_1 V_1 + p_2 V_2)/(V_1 + V_2).$$

THE ROLE OF ENTROPY IN PERFORMING WORK. The Kelvin principle rules out a cyclic process whose only result would be the complete conversion of a certain amount of heat into work as a result of contact with only one heat source. The formula for the efficiency of the Carnot cycle shows that the amount of heat taken from the source can be converted into work only partially, the portion of heat converted into work being larger for lower sink temperature. The physical reasons behind this are the requirements of the second law of thermodynamics. Since in any processes the entropy in closed systems increases, a certain amount of heat cannot be completely converted into work because this would mean the disappearance of the corresponding entropy, which is in contradiction to the second law of thermodynamics. Hence, when the work is done, at least the same entropy which was taken from the source must be transferred to the sink. The entropy taken from the source in the Carnot cycle is equal to $Q^{(+)} / T_1$, while the entropy transferred to the sink is $-Q^{(-)} / T_2$. It follows from what has been said above that we must always have

$$-Q^{(-)} / T_2 \geq Q^{(+)} / T_1,$$

or, in other words,

$$\frac{Q^{(+)}}{T_1} + \frac{Q^{(-)}}{T_2} \leq 0,$$

which coincides with (22.3). It is this circumstance that limits the efficiency of an engine.

The maximum efficiency is attained in a reversible machine, since in this case the minimum possible entropy is transferred to the sink. In order to increase the value of the maximum possible efficiency, we must either increase the temperature of the source or decrease the temperature of the

sink. The temperature of the sink cannot be lowered unlimitedly because of natural conditions existing in the surrounding atmosphere. Of course, we can artificially cool air, but work must be done for this purpose, and ultimately we would have no increase in efficiency. Hence we must assume that a certain minimum temperature T_0 is fixed for accomplishing work.

Suppose we have a cyclic engine to which some energy in the form of heat δQ has been supplied at a temperature T . The engine will transform into work a part of this energy, which under most favourable conditions is equal to

$$\delta W_{\max} = (1 - T_0/T) \delta Q. \quad (22.16)$$

The energy of the system available for consumption is the part of its energy which, when supplied to the engine in the form of heat at temperature T , is converted into work. If portions of heat δQ are supplied to an engine at different temperatures, the maximum energy converted into work is, according to (22.16), given by

$$W_{\max} = \int (1 - T_0/T) \delta Q. \quad (22.17)$$

The remaining energy, equal to the difference between the energy supplied to the engine in the form of heat and the energy converted into work, is inaccessible for conversion into work.

Suppose that the state of a system which converts its energy into work changes, and the system goes over from a state 1 to state 2. In this case, the maximum energy which can be converted into work also changes. Obviously, this change in the maximum accessible energy is given by

$$\Delta W_{\max} = \int_{(1)}^{(2)} (1 - T_0/T) \delta Q. \quad (22.18)$$

Moreover, we must assume that states 1 and 2 are related through a reversible process (this assumption must be made in integral (22.18) in order to retain the condition that the change in the accessible energy is maximum). Under these conditions, $\delta Q/T = dS$, and the integral can be easily evaluated:

$$\Delta W_{\max} = Q - T_0(S_2 - S_1).$$

This means that the additional energy constitutes only a part of energy Q which is supplied to the system in the form of heat, the difference between them being the larger the greater the change in entropy. This circumstance must be

taken into account while analyzing the devices which convert heat into work.

Example 22.1. Calculate the change in entropy when a monatomic ideal gas of mass m_1 , which has initial temperature T_1 and pressure p_1 , is mixed with a diatomic gas of mass m_2 at the initial temperature T_2 and pressure p_2 . Molar masses of the gases being mixed are M_1 and M_2 .

The initial volumes V_1 and V_2 of the gases can be found from the equation of state:

$$p_1 V_1 = \nu_1 R T_1, \quad p_2 V_2 = \nu_2 R T_2, \quad (22.19)$$

where $\nu_1 = m_1/M_1$ and $\nu_2 = m_2/M_2$ are the numbers of moles of the monatomic and diatomic gases. We can assume that the gases are mixed in two consecutive stages: isothermal expansion of each of the gases to the volume $V = V_1 + V_2$ and temperature equalization at constant volume. The final temperature attained as a result of temperature equalization is determined from the law of conservation of energy:

$$\nu_1 C_{V1} (T_1 - T) = \nu_2 C_{V2} (T - T_2), \quad (22.20)$$

whence

$$T = \frac{\nu_1 C_{V1} T_1 + \nu_2 C_{V2} T_2}{\nu_1 C_{V1} + \nu_2 C_{V2}}, \quad (22.21)$$

where C_{V1} and C_{V2} are molar heat capacities at constant volume.

In the general formula $T dS = dU + p dV$ we must put $dU = 0$ for isothermal expansion and $dV = 0$ for temperature equalization at constant volume, where $dU = \nu C_V dT$. Hence, the total change in entropy when the gases are mixed:

$$\begin{aligned} \Delta S &= \nu_1 R \int_{V_1}^V \frac{dV}{V} + \nu_1 C_{V1} \int_{T_1}^T \frac{dT}{T} + \nu_2 R \int_{V_2}^V \frac{dV}{V} + \nu_2 C_{V2} \int_{T_2}^T \frac{dT}{T} \\ &= \nu_1 R \ln \frac{V}{V_1} + \nu_1 C_{V1} \ln \frac{T}{T_1} + \nu_2 R \ln \frac{V}{V_2} + \nu_2 C_{V2} \ln \frac{T}{T_2}. \end{aligned} \quad (22.22)$$

Considering that

$$(V/V_1) = p_1 T / (p T_1), \quad (V/V_2) = p_2 T / (p T_2), \quad C_{V1} = 3R/2, \\ C_{V2} = 5R/2,$$

we find from (22.22)



Fig. 51. Expansion of a gas at constant pressure

$$\Delta S = v_1 R \ln \left[\frac{p_1}{p} \left(\frac{T}{T_1} \right)^{5/2} \right] + v_2 R \ln \left[\frac{p_2}{p} \left(\frac{T}{T_2} \right)^{7/2} \right]. \quad (22.23)$$

Example 22.2. Analyze the irreversible expansion of a gas at a constant external pressure. Two cylinders *A* and *B* are connected by a thin tube having a stopcock *C* (Fig. 51). Cylinder *A* with a volume *V* is closed and contains *v* moles of a monatomic ideal gas under a pressure $p > p_0$. The open end of cylinder *B* is in contact with atmosphere at pressure p_0 . Cylinder *B* has a piston which can slide without friction along its walls. At first the piston is in the extreme left position. Then the stopcock *C* in the tube between the cylinders is slightly opened, and the gas from cylinder *A* slowly flows to cylinder *B*. As a result, the piston of cylinder *B* moves infinitely slowly to the right. Gases in the cylinders exchange heat with the surrounding medium which is at a constant temperature T_0 . Find the number of moles of the gas flowing from cylinder *A* to cylinder *B* before the system attains equilibrium. Determine the ratio of volume V_B of the gas in cylinder *B* in front of the piston to the volume *V*, the work *A* performed by the gas, and the amount of heat *Q* exchanged by the gas with the ambient. Calculate the total change ΔS in the entropy of the gas and surrounding medium.

Since the gas expands isothermally, we can write

$$pV = p_0(V + V_B), \text{ i.e. } p = p_0(1 + V_B/V), \quad (22.24)$$

whence

$$V_B/V = p/p_0 - 1. \quad (22.25)$$

In order to find the number *x* of moles transferred as a result of expansion to the volume of cylinder *B*, we write the equations of state for the initial and final states: $pV = vRT_0$, $p_0V = (v - x)RT_0$,

from which it follows that

$$x = v(1 - p_0/p). \quad (22.26)$$

The work of the gas upon expansion is $A = p_0 V_B$, or (see (22.26) and (22.25))

$$A = (p - p_0) V = p V x / v = x R T_0, \quad (22.27)$$

i.e. during expansion the gas performs work on the surrounding medium. Since this process is isothermal, the internal energy of the (ideal) gas has not changed, and hence the entire energy spent for performing work was obtained by the gas from the surrounding medium in the form of heat. According to the law of conservation of energy, this amount of heat is equal to

$$Q = A = x R T_0, \quad (22.28)$$

i.e. the heat was supplied to the gas from the surrounding medium.

The total change in entropy is the sum of the change ΔS_g in the entropy of the gas and the change ΔS_m in the entropy of the medium:

$$\Delta S = \Delta S_g + \Delta S_m. \quad (22.29)$$

To calculate the change in entropy, we replace the irreversible process under consideration by a reversible one with the same final state. This will be isothermal expansion of the gas:

$$\Delta S_g = \int_{(1)}^{(2)} \delta Q / T = \nu R \ln (p / p_0). \quad (22.30)$$

The surrounding medium transfers to the gas the amount of heat $Q = x R T_0$, hence its heat decreases by $-Q = -x R T_0$, and its entropy changes by

$$\Delta S_m = -Q / T_0 = -x R, \quad (22.31)$$

i.e. its value decreases. The total change in entropy as a result of the process considered above is

$$\Delta S = \nu R \ln (p / p_0) - x R = \nu R \{ \ln [v / (v - x)] - x / v \}, \quad (22.32)$$

where $p / p_0 = v / (v - x)$.

Example 22.3. Find the work performed by a gas expanding reversibly and isothermally from volume V and pressure p to pressure p_0 and volume $V + V_B$ (see Example 22.2). Compare this work with the work (22.27) of the irreversible process and express the difference between them in terms of the change in entropy.

The work done during isothermal expansion of the gas is

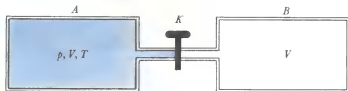


Fig. 52. Expansion of a gas into vacuum

equal to

$$\begin{aligned}
 A_{\text{rev}} &= \int_{(1)}^{(2)} p \, dV = \nu R T_0 \int_{(1)}^{(2)} dV/V = \nu R T_0 \ln [(V + V_B)/V] \\
 &= \nu R T_0 \ln (p/p_0) = \nu R T_0 \ln [v/(v-x)].
 \end{aligned}$$

Taking (22.27) into account, we find

$$A - A_{\text{rev}} = x R T_0 - \nu R T_0 \ln [v/(v-x)] = -T_0 \Delta S, \quad (22.33)$$

i.e. the work done in the irreversible process is smaller than in the reversible process.

Example 22.4. Investigate the irreversible expansion of a gas into free space. Given two cylinders *A* and *B* of the same volume, connected by a tube with a stopcock *C* (Fig. 52). The walls of the cylinders (and the tube) are assumed to be adiabatic. At first, the stopcock *C* is closed, cylinder *B* is empty, and cylinder *A* contains ν moles of the gas at temperature T . The stopcock *C* is then slightly opened, and the gas flows through the tube from *A* to *B*. This process is supposed to be sufficiently slow to assume that the gas in cylinder *A*, as well as in *B*, is in quasistatic equilibrium. However, it must not be so slow that the cylinders can exchange heat directly. In other words, we neglect the heat exchange between the cylinders. When the pressure in the two cylinders becomes equal to p' , the stopcock is closed. Find the number of moles transferred from cylinder *A* to cylinder *B*, the temperatures T'_A and T'_B in cylinders *A* and *B*, pressure p' , and the change ΔS of the entropy in this process.

In this initial state, cylinder *A* contains ν moles of the gas under pressure p and temperature $T = pV/(\nu R)$ in volume V , and in the final state, $\nu - x$ moles of the gas at pressure p' and temperature T'_A . The amount of substance has changed in this process, hence in order to be able to use formulas valid for a constant amount of substance, we must recalculate the final state for ν moles of the gas at the same temperature and pressure. Obviously, if $\nu - x$ moles of the gas fill the volume

V , v moles of the gas will occupy the volume $vV/(v-x)$. Hence the final state of the gas in cylinder A is characterized by the parameters p' , $vV/(v-x)$, and T_A' . The transition from the initial to the final state is adiabatic, and hence we can write the relation (see (18.8))

$$T_A' \left(V \frac{v}{v-x} \right)^{\gamma-1} = TV^{\gamma-1}, \quad (22.34)$$

whence

$$T_A' = T(1-x/v)^{\gamma-1}. \quad (22.35)$$

On the other hand, the equation for the ideal gas in the final state has the form

$$p'V = (v-x)PT_A' \quad (22.36)$$

for cylinder A , and

$$p'V = xRT_B' \quad (22.37)$$

for cylinder B . Comparing (22.36) and (22.37), we get

$$(v-x)T_A' = xT_B'. \quad (22.38)$$

Since the process is adiabatic and no work is done, the internal energy of the gas remains unchanged. In other words, the change in the internal energy of the gas in the process is equal to zero:

$$\Delta U = (v-x)C_V(T_A' - T) + xC_V(T_B' - T) = 0. \quad (22.39)$$

Taking into account relation (22.38), we obtain

$$T_A' = vT/[2(v-x)], \quad (22.40)$$

$$T_B' = vT/(2x). \quad (22.41)$$

Thus, the gas in cylinders A and B is not in thermal equilibrium. The value of x can be found from the equation which is obtained by equating the right-hand sides of Eqs. (22.40) and (22.35):

$$vT/[2(v-x)] = T(1-x/v)^{\gamma-1}. \quad (22.42)$$

Solving this equation for x , we obtain

$$x = v(1 - 2^{-1/\gamma}). \quad (22.43)$$

The pressure p' of the final state is obtained from Eq. (22.37) into which we substitute expression (22.41) for T_B' :

$$p' = xRT_B'/V = vRT/(2V) = p/2. \quad (22.44)$$

It should be recalled that the change in the entropy of v moles of an ideal gas upon a change in pressure by dp and in temperature by dT is equal to

$$dS = \frac{\delta Q}{T} = vC_p \frac{dT}{T} - vR \frac{dp}{p}. \quad (22.45)$$

Consequently, the change in the entropy of $v-x$ moles of the gas in cylinder A and v moles of the gas in cylinder B are respectively given by

$$\Delta S_A = (v-x)C_p \ln(T'_A/T) - (v-x)R \ln(p'/p), \quad (22.46)$$

$$\Delta S_B = xC_p \ln(T'_B/T) - xR \ln(p'/p). \quad (22.47)$$

Then the total change in the gas entropy is

$$\begin{aligned} \Delta S = \Delta S_A + \Delta S_B = C_p [(v-x) \ln(T'_A/T) + x \ln(T'_B/T)] \\ + vR \ln(p/p'). \end{aligned} \quad (22.48)$$

Sec. 23. THERMODYNAMIC FUNCTIONS AND THE CONDITIONS OF THERMODYNAMIC STABILITY

The basic relations for thermodynamic functions are derived and used to analyze the thermodynamic stability criteria under different conditions. The set of experimental data required for a complete thermodynamic description of a substance is considered. The Le Chatelier-Braun principle is formulated.

SOME MATHEMATICAL FORMULAS. Suppose that we have three variables connected through a certain relation

$$z = z(x, y). \quad (23.1a)$$

This means that only two of these variables are independent, while the third is a function of the first two. This dependence is expressed in (23.1a) in such a form that x and y are independent variables, while z is a function of these variables. However, Eq. (23.1a) can be solved for x or for y , and the relation between x , y , and z can be written in the form

$$x = x(y, z); \quad y = y(z, x). \quad (23.1b)$$

Here y , z or z , x are respectively taken as independent variables. Thus, the independent quantities can be chosen arbitrarily.

The total differentials of z , x , and y defined by formulas (23.1a) and (23.1b) for different pairs of quantities taken as independent variables can be written as follows:

$$\begin{aligned} dz = \frac{\partial z}{\partial x} dx + \frac{\partial z}{\partial y} dy, \quad dy = \frac{\partial y}{\partial x} dx + \frac{\partial y}{\partial z} dz, \\ dx = \frac{\partial x}{\partial y} dy + \frac{\partial x}{\partial z} dz. \end{aligned} \quad (23.2)$$

In thermodynamics, we often deal with total differentials of various functions of state, taking different pairs of variables as independent. Suppose, for example, that we have a certain function F which can be treated as a function of x , y or as a function of x , z . Its total differentials for these two cases have the following form:

$$dF = \frac{\partial F}{\partial x} dx + \frac{\partial F}{\partial y} dy, \quad (23.3a)$$

$$dF = \frac{\partial F}{\partial x} dx + \frac{\partial F}{\partial z} dz. \quad (23.3b)$$

Expression (23.3a), as well as (23.3b), contain the same factor $\partial F/\partial x$. However, the meaning and the values of this quantity are quite different: in the first case, it is the partial derivative for constant y , while in the second, for constant z . In order to avoid misunderstanding, in thermodynamics it is explicitly indicated which independent variables were used while calculating a derivative. For example, formulas (23.3) should be written as follows:

$$dF = \left(\frac{\partial F}{\partial x} \right)_y dx + \left(\frac{\partial F}{\partial y} \right)_x dy, \quad (23.4a)$$

$$dF = \left(\frac{\partial F}{\partial x} \right)_z dx + \left(\frac{\partial F}{\partial z} \right)_x dz. \quad (23.4b)$$

No misunderstanding is possible in this case, and it is clear that

$$\left(\frac{\partial F}{\partial x} \right)_y \neq \left(\frac{\partial F}{\partial x} \right)_z.$$

This condition can be used to obtain from (23.2) the following relation between partial derivatives:

$$\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x \left(\frac{\partial z}{\partial x} \right)_y = -1. \quad (23.5)$$

If we know that $d\Phi$ is a total differential and can be written in the form

$$d\Phi = P dx + Q dy, \quad (23.6)$$

where P and Q are some known functions of x and y , it follows from the definition and the properties of the total

differential that

$$P = \left(\frac{\partial \Phi}{\partial x} \right)_y, \quad Q = \left(\frac{\partial \Phi}{\partial y} \right)_x, \quad \left(\frac{\partial P}{\partial y} \right)_x = \left(\frac{\partial Q}{\partial x} \right)_y. \quad (23.7)$$

DEFINITION OF A THERMODYNAMIC FUNCTION. A function of state is called a **thermodynamic function** or **thermodynamic potential**. There is an infinitely large number of thermodynamic functions, since if one of them is known, any function of this function will also be a thermodynamic function of state (we do not discuss here some limitations which must be imposed on the choice of the functions). In addition to p , V , and T , which characterize a state, we know from the above discussion such functions of state as the internal energy U , enthalpy H , and entropy S . The internal energy was considered in Sec. 14, the enthalpy was defined by (17.7), and the entropy in the general case is determined by the Boltzmann formula (19.2). As regards entropy, we must add a few words about it.

Let a system in equilibrium consist of two subsystems. The entropies of the system and the subsystems are given by

$$S = k \ln \Gamma, \quad S_1 = k \ln \Gamma_1, \quad S_2 = k \ln \Gamma_2. \quad (23.8)$$

The quantities Γ , Γ_1 and Γ_2 are related to the probabilities for the system and subsystems through the formulas of the form (5.1). According to the probability multiplication rule for independent events, we have

$$\Gamma = \Gamma_1 \Gamma_2. \quad (23.9)$$

Taking logarithms of (23.9) and allowing for (23.8), we find

$$S = S_1 + S_2,$$

i.e. entropy is an additive function of state: the entropy of the system is equal to the sum of entropies of its components.

THERMODYNAMIC IDENTITY. For reversible processes in which $\delta Q = TdS$, the second law of thermodynamics assumes the form

$$TdS = dU + p dV. \quad (23.10)$$

This equality is a **thermodynamic identity**, since it is identically valid for all reversible processes.

FREE ENERGY, OR HELMHOLTZ' FUNCTION. Besides the thermodynamic functions listed above, only a few functions among an infinitely large number of functions of state play

an important role in thermodynamics. The most important among these is the free energy F introduced by Helmholtz in 1882.

Let us rewrite (23.10) in the form

$$\delta A = p dV = -dU + TdS.$$

The work performed by a system in an isothermal process ($T = \text{const}$) can be represented as

$$\delta A = -d(U - TS) = -dF. \quad (23.11)$$

Thus, the infinitely small work performed by a system in an isothermal process is a total differential and is equal to the change in the free energy taken with the opposite sign:

$F = U - TS.$

(23.12)

Clearly, free energy is a function of state since, according to (23.12), it is a function of the functions of state. Consequently, in isothermal processes it plays the role of the potential energy: its variation taken with the opposite sign is equal to the work performed. But this is true only for an isothermal process. In an arbitrary process the work is generally not equal to the change in the free energy.

GIBBS' THERMODYNAMIC FUNCTION. This function is defined by

$G = F + pV = H - TS.$

(23.13)

Sometimes it is called the **Gibbs thermodynamic potential**.

MAXWELL THERMODYNAMIC RELATIONS. Each of the thermodynamic functions U , H , F , and G can be represented as a function of any two independent variables from p , V , T , and S , S being introduced by the thermodynamic identity (23.10) as an independent variable. In other words, p , V , T , and S are connected through two relations, viz. the equation of state and the thermodynamic identity, therefore only two of them can be independent.

Let us calculate the total differentials of the thermodynamic functions. The total differential dU is determined from formula (23.10):

$$dU = TdS - pdV. \quad (23.14)$$

Other differentials can be easily calculated:

$$dH = dU + p dV + V dp = T dS + V dp, \quad (23.15)$$

$$dF = -S dT - p dV, \quad (23.16)$$

$$dG = -S dT + V dp, \quad (23.17)$$

where we used the expression (23.14) for dU . Combining (23.7), and (23.14) to (23.17), we obtain:

$$\begin{aligned} T &= \left(\frac{\partial U}{\partial S} \right)_V, \quad -p = \left(\frac{\partial U}{\partial V} \right)_S, \quad \left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial p}{\partial S} \right)_V, \\ T &= \left(\frac{\partial H}{\partial S} \right)_p, \quad V = \left(\frac{\partial H}{\partial p} \right)_S, \quad \left(\frac{\partial T}{\partial p} \right)_S = \left(\frac{\partial V}{\partial S} \right)_p, \\ -S &= \left(\frac{\partial F}{\partial T} \right)_V, \quad -p = \left(\frac{\partial F}{\partial V} \right)_T, \quad \left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V, \\ -S &= \left(\frac{\partial G}{\partial T} \right)_p, \quad V = \left(\frac{\partial G}{\partial p} \right)_T, \quad - \left(\frac{\partial S}{\partial p} \right)_T = \left(\frac{\partial V}{\partial T} \right)_p. \end{aligned} \quad (23.18)$$

The four equalities between the derivatives in (23.18) are called **Maxwell's thermodynamic relations**.

ANOTHER FORM OF DIFFERENTIALS OF INTERNAL ENERGY, ENTHALPY, AND ENTROPY. In various applications it is sometimes necessary to represent the differentials dU , dH and dS in a form different from (23.14), (23.15), and (23.10). It is assumed that the internal energy of a substance is a function of only temperature and volume, i.e. $U = U(T, V)$, and hence

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV = C_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV, \quad (23.19a)$$

where, by definition, $C_V = (\partial U / \partial T)_V$. It follows from (23.10) and (23.19a) that

$$dS = \frac{dU}{T} + \frac{p}{T} dV = C_V \frac{dT}{T} + \left[\frac{1}{T} \left(\frac{\partial U}{\partial V} \right)_T + \frac{p}{T} \right] dV. \quad (23.19b)$$

On the other hand, treating entropy as a function of T and V , viz. $S = S(T, V)$, we obtain

$$dS = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV. \quad (23.20)$$

Comparing (23.19b) and (23.20), we get

$$\frac{C_V}{T} = \left(\frac{\partial S}{\partial T} \right)_V, \quad \left(\frac{\partial S}{\partial V} \right)_T = \frac{1}{T} \left[\left(\frac{\partial U}{\partial V} \right)_T + p \right]. \quad (23.21)$$

Using the Maxwell relation $(\partial S / \partial V)_T = (\partial p / \partial T)_V$, we can transform the second of these equalities as follows:

$$(\partial U / \partial V)_T = T(\partial p / \partial T)_V - p. \quad (23.22)$$

With the help of this formula, expression (23.19a) can be written in the form

$$dU = C_V dT + [T(\partial p / \partial T)_V - p] dV. \quad (23.23)$$

Similar calculations lead to the following expressions for the differentials of entropy and enthalpy:

$$dS = C_V \frac{dT}{T} + \left(\frac{\partial p}{\partial T} \right)_V dV, \quad (23.24)$$

$$dH = C_p dT + \left[V - T \left(\frac{\partial V}{\partial T} \right)_p \right] dp. \quad (23.25)$$

In the last expression, $C_p = (\partial H / \partial T)_p$ by definition.

If we take T and p as independent variables, we obtain the following expression for the differential of entropy:

$$dS = C_p \frac{dT}{T} - \left(\frac{\partial V}{\partial T} \right)_p dp. \quad (23.26)$$

FORMULAS FOR HEAT CAPACITIES. Equating the right-hand sides of expressions (23.24) and (23.26) for dS , we obtain

$$C_V \frac{dT}{T} + \left(\frac{\partial p}{\partial T} \right)_V dV = C_p \frac{dT}{T} - \left(\frac{\partial V}{\partial T} \right)_p dp, \quad (23.27)$$

whence

$$C_p - C_V = T \left[\left(\frac{\partial p}{\partial T} \right)_V \frac{dV}{dT} + \left(\frac{\partial V}{\partial T} \right)_p \frac{dp}{dT} \right], \quad (23.28)$$

where $C_p - C_v$ behaves in a similar way both when the volume is changed at $p = \text{const}$ and when the pressure is changed at $V = \text{const}$. This can be immediately seen from (23.28), since

$$(C_p - C_v)_V = T \left(\frac{\partial V}{\partial T} \right)_p \left(\frac{\partial p}{\partial T} \right)_V, \quad (23.29)$$

$$(C_p - C_v)_p = T \left(\frac{\partial p}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_p.$$

Relation (23.5) for the variables V , p , and T has the form

$$\left(\frac{\partial p}{\partial T} \right)_V = - \left(\frac{\partial V}{\partial T} \right)_p \left(\frac{\partial p}{\partial V} \right)_T. \quad (23.30)$$

Hence formula (23.28) allowing for (23.29) and (23.30) is finally written as

$$C_p - C_v = -T \frac{(\partial V / \partial T)_p^2}{(\partial V / \partial p)_T}. \quad (23.31)$$

EXPERIMENTAL DATA REQUIRED FOR COMPLETE THERMODYNAMIC DESCRIPTION OF A SUBSTANCE. Formula (23.31) in combination with previously obtained formulas for dU , dH , and dS allows us in principle to determine U , H , and S only if p , V , T , and one of the heat capacities C_v or C_p are given. On the other hand, the free energy F and the Gibbs function G are expressed in terms of U , H , and S and hence they can also be determined. Thus, the properties of a substance, which must be measured in order to describe all its thermodynamic properties are fixed. It is appropriate to note that we are speaking only of pure substances.

When we consider a pure substance in a certain phase (for example, in the form of vapour or liquid), we can assume that there exists an equation of state $p = p(T, V)$ for it, which in principle can be established experimentally, after a sufficiently large number of measurements, or theoretically, at least approximately. Then the information about heat capacities must be experimentally obtained. Together with Eq. (23.31) these data give a complete quantitative description of all thermodynamic characteristics of the substances. In this way, thermodynamic tables for real substances are obtained.

THE MAIN CRITERION OF THERMODYNAMIC STABILITY. In an adiabatically isolated system, the equilibrium state is attained at the maximum entropy. This means

that all the states that are infinitely close to this state and to which the system can go over without a supply or removal of heat have lower entropy. The second law of thermodynamics prohibits transitions to such states, and hence the state of an adiabatically isolated system is stable at the maximum entropy of the system.

The general theory of thermodynamic stability was worked out in 1875–1878 by the American physicist J. Gibbs who formulated the following necessary and sufficient conditions for stability of an isolated system:

(1) in all possible changes in the state of a system, which do not affect its energy, the entropy variation either vanishes or is negative;

(2) in all possible changes of the state of a system, which do not affect its entropy, the variation of its energy is either vanishing or positive.

On the basis of these general conditions, Gibbs also considered particular cases and proposed a theory of thermodynamic potential.

STABILITY CRITERION FOR A SYSTEM WITH CONSTANT VOLUME AND ENTROPY. The Clausius inequality (22.7), combined with (22.11), for an infinitely small irreversible process occurring in a system has the form

$$\delta Q < T dS. \quad (23.32)$$

Taking the first law of thermodynamics into account, this condition can be written as

$$dU + p dV - T dS < 0. \quad (23.33)$$

In the case of constant entropy ($dS = 0$) and volume ($dV = 0$), this gives

$$dU < 0, \quad (23.34)$$

i.e. only the processes accompanied by a decrease in the internal energy can occur in the system. Consequently, the state with the minimum internal energy is stable.

STABILITY CRITERION FOR A SYSTEM WITH CONSTANT PRESSURE AND ENTROPY. In this case, condition (23.33) has the form

$$d(U + pV) < 0, \quad (23.35)$$



The state of an adiabatically isolated system is stable when the entropy of the system is maximum.

The state of a system with constant volume and entropy is stable when the internal energy is minimum.

The state of a system with constant pressure and entropy is stable when the enthalpy of the system is minimum.

The state of a system with constant volume and temperature is stable when the free energy is minimum. The state of a system with constant temperature and pressure is stable when the thermodynamic potential is minimum.

i.e. only processes accompanied by a decrease in the enthalpy $H = U + pV$ can occur in the system. Consequently, the state with the minimum enthalpy is stable.

STABILITY CRITERION FOR A SYSTEM WITH CONSTANT VOLUME AND TEMPERATURE. When $dV = 0$ and $T = \text{const}$, inequality (23.33) becomes

$$d(U - TS) < 0, \quad (23.36)$$

i.e. only processes accompanied by a decrease in the free energy $F = U - TS$ can occur in the system. Consequently, the state with the minimum free energy is stable.

STABILITY CRITERION FOR A SYSTEM WITH CONSTANT TEMPERATURE AND PRESSURE. Using expression (23.13) for thermodynamic potential, inequality (23.33) is transformed to

$$dG - SdT + Vdp < 0. \quad (23.37)$$

At constant temperature and pressure, $dT = 0$ and $dp = 0$, and (23.37) is reduced to the inequality

$$dG < 0, \quad (23.38)$$

i.e. only processes accompanied by a decrease in the thermodynamic potential can occur in the system. Hence the state with the minimum thermodynamic potential is stable.

LE CHATELIER-BRAUN PRINCIPLE.* The stability of a state is ensured by the factors which appear in the system when the equilibrium is disturbed, and which tend to return it to the equilibrium state. The appearance of these factors is necessitated by the existence of stable states. In electrodynamics, this statement is formulated as Lenz's law. In thermodynamics, it is expressed as the Le Chatelier-Braun principle: when a system in stable thermodynamic equilibrium is acted upon by external factors that tend to disturb this state, processes emerge in the system, tending to eliminate the changes introduced by the external effects.

* This principle was formulated in 1884 by the French scientist Le Chatelier (1850-1936) and later in 1887, in a more general form, by the German scientist Braun (1850-1918).

THERMODYNAMIC FUNCTIONS IN TERMS OF PARTITION FUNCTION. If expression (7.15) for the mean energy does not contain the kinetic energy of the general ordered translatory motion of molecules, i.e. if the centre of mass is at rest, this expression can be used as statistical definition of the internal energy. Considering that Z is a function of temperature and volume, and $\beta = 1/(kT)$, the derivative with respect to β in this expression can be assumed to be taken at constant volume:

$$U = - \left(\frac{\partial \ln Z}{\partial \beta} \right)_V = \left(\frac{\partial \ln Z}{\partial T} \right)_V kT. \quad (23.39)$$

Let us write formula (23.16), taking into account the expression for S from (23.12) in the form

$$dF = -(U - F)dT/T - p dV \quad (23.40a)$$

and compare it with the differential of the expression $(-kT \ln Z)$ considering that it depends only on T and V :

$$d(-kT \ln Z) = \left(-kT \frac{\partial \ln Z}{\partial T} - k \ln Z \right) dT - \frac{\partial (kT \ln Z)}{\partial V} dV. \quad (23.40b)$$

Expressions (23.40a) and (23.40b) are identical if the internal energy is determined by expression (23.39) and the free energy is given by

$$F = -kT \ln Z. \quad (23.41)$$

The remaining thermodynamic functions are expressed in terms of the free energy through formulas (23.18):

$$p = - \left(\frac{\partial F}{\partial V} \right)_T; \quad \text{pressure}$$

$$S = - \left(\frac{\partial F}{\partial T} \right)_V = k \ln Z + kT \left(\frac{\partial \ln Z}{\partial T} \right)_V; \quad \text{entropy} \quad (23.42a)$$

internal energy

$$U = F - T \left(\frac{\partial F}{\partial T} \right)_V = kT^2 \left(\frac{\partial \ln Z}{\partial T} \right)_V; \quad (23.42b)$$

enthalpy

$$H = U + pV; \quad (23.42c)$$

temperature and volume

$$T = \left(\frac{\partial H}{\partial S} \right)_p, \quad V = \left(\frac{\partial H}{\partial p} \right)_S; \quad (23.42d)$$

Gibbs' thermodynamic function

$$G = F + pV = H - TS. \quad (23.42e)$$

Thus, the knowledge of the partition function makes it possible to carry out the complete analysis of the thermodynamic state of a system.

Example 23.1. Using the partition function, find the thermodynamic functions of a monatomic ideal gas.

In Example 12.1, the partition function of a monatomic ideal gas was calculated in the form of (12.25). Taking into account expression (23.41) for the free energy and formula (12.26), we arrive at the expression

$$F = -nkT \left\{ \ln \left[\frac{V(2\pi mkT)^{3/2}}{n(2\pi\hbar)^3} \right] + 1 \right\}. \quad (23.43)$$

According to (23.42a), the entropy is equal to

$$S = -(\partial F / \partial T)_V = nk \left\{ \ln \left[\frac{V(2\pi mkT)^{3/2}}{n(2\pi\hbar)^3} \right] + \frac{5}{2} \right\}. \quad (23.44)$$

In accordance with (23.42b), the internal energy is given by

$$U = kT^2 \left(\frac{\partial \ln Z}{\partial T} \right)_V = 3/2 nkT. \quad (23.45)$$

The pressure can be calculated by using (23.42a):

$$p = - \left(\frac{\partial F}{\partial V} \right)_T = \frac{nkT}{V} = \frac{\nu N_A kT}{V} = \frac{\nu RT}{V}, \quad (23.46)$$

where $\nu = n/N_A$ is the number of moles. The enthalpy and the Gibbs thermodynamic function are found with the help of (23.42c) and (23.42e).

Example 23.2. Find the change in the entropy after mixing of two monoatomic gases of mass m_1 and m_2 , which initially occupied volumes V_1 and V_2 at temperatures T_1 and T_2 respectively.

We shall split the mixing into two consecutive processes: the isothermal expansion of each of the two volumes V_1 and V_2 to the final volume $V = V_1 + V_2$ and the temperature equalization at constant volume. For the initial state we have

$$p_1 V_1 = \nu_1 R T_1, \quad p_2 V_2 = \nu_2 R T_2, \quad (23.47)$$

where $\nu_1 = m_1/M$ and $\nu_2 = m_2/M$ are the numbers of moles in each of the portions being mixed, and M is the molar mass of the gas. After the temperature and pressure level out and equilibrium sets in, we get

$$pV = \nu R T, \quad V = V_1 + V_2, \quad \nu = \nu_1 + \nu_2. \quad (23.48)$$

Using the law of conservation of energy for temperature equalization, we obtain the following expression for the final temperature:

$$T = (\nu_1 T_1 + \nu_2 T_2) / (\nu_1 + \nu_2). \quad (23.49)$$

Considering the relations $V = \nu R T / p$ and $n = \nu N_A$, we transform expression (23.44) for entropy to

$$S = \nu R \left\{ \ln \left[\frac{kT}{p} \frac{(2\pi mkT)^{3/2}}{(2\pi\hbar)^3} \right] + \frac{5}{2} \right\}. \quad (23.50)$$

The change in the entropy of the first mass of the gas is the sum of two components: the change in the entropy during the gas expansion to the final volume and pressure, and during the subsequent change in temperature to the final value T :

$$\begin{aligned} \Delta S_1 &= \nu_1 R \left\{ \ln \left[\frac{kT}{p} \frac{(2\pi mkT)^{3/2}}{(2\pi\hbar)^3} \right] + \frac{5}{2} \right\} \\ &\quad - \nu_1 R \left\{ \ln \left[\frac{kT_1}{p_1} \frac{(2\pi mkT_1)^{3/2}}{(2\pi\hbar)^3} \right] + \frac{5}{2} \right\} \\ &= \nu_1 R \ln \left[\frac{p_1}{p} \left(\frac{T}{T_1} \right)^{5/2} \right]. \end{aligned} \quad (23.51)$$

The change in entropy ΔS_2 is calculated in a similar way. The total change in the entropy upon mixing the gases is

$$\begin{aligned}\Delta S = \Delta S_1 + \Delta S_2 = & v_1 R \ln \left[\frac{p_1}{p} \left(\frac{T}{T_1} \right)^{5/2} \right] \\ & + v_2 R \ln \left[\frac{p_2}{p} \left(\frac{T}{T_2} \right)^{5/2} \right].\end{aligned}\quad (23.52)$$

PROBLEMS

- 2.1. Using the law of equipartition of energy, find the internal energy of 2 l of hydrogen and 3 l of carbon dioxide under pressure of 10^5 Pa.
- 2.2. A gas expands polytropically, the polytropic exponent being $n=2$. The initial parameters are $T_0 = 350$ K, $p_0 = 19.6 \times 10^5$ Pa, and $V_0 = 5$ l. The final pressure $p = 1.96 \times 10^5$ Pa. Find the final temperature and volume of the gas.
- 2.3. One kilomole of an ideal gas under normal conditions ($p_0 = 101.3$ kPa, $T_0 = 273.15$ K) is compressed in a polytropic process with the polytropic exponent $n = 1.25$ to half of the initial volume. Find the final pressure and temperature.
- 2.4. Calculate the free energy F , entropy S , and enthalpy H for 1 m³ of helium at temperature 1227°C and pressure 100 Pa.
- 2.5. Calculate the change in the free energy and entropy of 50 cm³ of helium upon adiabatic expansion to 100 cm³, if the initial temperature and pressure of helium were 1227°C and 100 Pa respectively.
- 2.6. Find the change in the free energy and entropy of 50 cm³ of helium upon an isothermal expansion to 100 cm³, if the initial temperature and pressure were 1500 K and 100 Pa.
- 2.7. 28 g of nitrogen at the temperature 127°C and pressure 0.98×10^5 Pa and 64 g of oxygen at 27°C and the same pressure are mixed at constant pressure. The temperature of gases becomes equal. (The vibrational degrees of freedom are ineffective in this temperature interval.) Find the change in the entropy and temperature of the mixture in the equilibrium state.
- 2.8. 1 mole of nitrogen molecules at the initial pressure 0.98×10^5 Pa are mixed with 2 moles of oxygen molecules at the initial pressure 1.96×10^5 Pa. The temperature of gases is the same and equal to 300 K. Find the change in entropy upon mixing.
- 2.9. An ideal gas is compressed so that its internal energy does not change. Find its molar heat capacity.
- 2.10. Analyze the behaviour of the thermodynamic functions of a spin system, calculated in Example 23.3, at a negative thermodynamic temperature.
Hint. Use the tables for hyperbolic functions.
- 2.11. One mole of molecules of an ideal gas of mass m is contained in a cylindrical vessel of height h in the gravitational field. Find the

- heat capacity of the gas in the vessel (provided that $mgh \ll kT$).
- 2.12. Molecules of a diatomic gas start dissociating as a result of a certain process. Find the increase in the gas pressure if 10% of molecules dissociate at a constant temperature.
- 2.13. Find the concentration of ideal gas molecules at $T = 290$ K and $p = 10^5$ Pa.

ANSWERS

- 2.1. $U_{H_2} = 490$ J; $U_{CO_2} = 882$ J. 2.2. $V = (p_0/p)^{1/\alpha} V_0 = 15.8$ l; $T = [pV/(p_0 V_0)] T_0 = 110.6$ K. 2.3. $p = 2.33 \cdot 10^5$ Pa; $T = 324.8$ K. 2.4. $F = -2460$ J; $S = 1.7$ J/K; $H = 250$ J. 2.5. $\Delta F = 0.0455$ J, $\Delta S = 0$. 2.6. $\Delta F = -0.00345$ J; $\Delta S = 2.3 \cdot 10^{-6}$ J/K. 2.7. $\Delta S = 8.3$ J/K; $t = 60.3$ °C. 2.8. $\Delta S = 17.3$ J/K. 2.9. $C = -C_V$. 2.11. $C = C_V + (R/12)[mgh/(kT)]^2$. 2.12. 10%. 2.13. $2.5 \cdot 10^{25} \text{ m}^{-3}$.
-



Electron and Photon Gases

Basic idea: Identical microparticles are indistinguishable by definition. Indistinguishable particles can be of two different types: (1) the particles whose number is arbitrary in a given quantum-mechanical state and (2) those whose number cannot exceed unity in a given state (i.e. either 0 or 1).

Analogy: Not more than one impenetrable solid can be present at the same time in the same region of space. If, however, such objects are, for example, clouds of vapour or smoke, several of them can simultaneously exist in the same region of space.

Sec. 24. VARIOUS MODELS OF THE BEHAVIOUR OF PARTICLES

The dependence of the model of particle behaviour on their properties is considered. The concept of indistinguishability of particles is analyzed. The nature of the statistic dependence on the particle behaviour model is discussed, and a general description of various models is given.

MAXWELL-BOLTZMANN MODEL. When considering a many-particle system, it was assumed (see Chap. 1) that they have some properties which make it possible to distinguish between them, although the particles were considered to be identical. Accordingly, two microscopic states differing only in that two particles exchanged places were assumed to be different while calculating the number of microscopic states. Such a model of distinguishable particles is called the **Maxwell-Boltzmann model**, and the statistical theory based on this model is called the **Maxwell-Boltzmann statistics**.

INDISTINGUISHABILITY OF PARTICLES. The properties which could be used to distinguish between two particles are unknown since the particles are quite identical by definition. Suppose that there are two identical particles in certain states. Obviously, the physical situation will not change if these particles interchange places. If we take two electrons, their indistinguishability is even more obvious because considerations about a possible difference in their internal states are irrelevant. If we assume that particles are indistinguishable, the rules for counting the microscopic

states will be different from those used in the Maxwell-Boltzmann model.

BOSE-EINSTEIN AND FERMI-DIRAC MODELS. Models in which particles are treated as indistinguishable are called the Bose-Einstein and Fermi-Dirac models.

These models differ in the particle behaviour with respect to microscopic states. If no two identical particles can be in a given state, we have the Fermi-Dirac model, while the Bose-Einstein model permits an arbitrary number of particles in the same state. It should be emphasized that the state is characterized not only by energy but by other parameters as well. For example, the states having the same energy but different directions of the momentum of particles are different. Hence, the above statement can be formulated more exactly: each quantum-mechanical state in the Bose-Einstein model can contain an arbitrary number of particles, while in the Fermi-Dirac model, not more than one particle can be present in any state.

The statistical theory based on the Bose-Einstein model is called the Bose-Einstein statistics.

The statistical theory based on the Fermi-Dirac model is called the Fermi-Dirac statistics.

FORMULAS OF THE MAXWELL-BOLTZMANN STATISTICS AS A LIMITING CASE OF THE BOSE-EINSTEIN AND FERMI-DIRAC STATISTICS. Real particles are indistinguishable and hence do not fit the Maxwell-Boltzmann model. They obey either the Bose-Einstein or the Fermi-Dirac statistics. Pauli showed that the particles with integral spins obey the Bose-Einstein statistics, while those with half-integral spins obey the Fermi-Dirac statistics. Although there are no particles obeying the Maxwell-Boltzmann statistics, it correctly describes the behaviour of particles in the most important cases which are encountered in practice. This is so because the formulas of the Bose-Einstein and Fermi-Dirac statistics are reduced to the formulas of the Maxwell-Boltzmann statistics when the number of states available for particles is much larger than the number of particles which can occupy these states, i.e. when the average number of particles per state is small.

This is the situation that is encountered most frequently in practice.

It should be remarked that in the limiting case the formulas become identical but it would be wrong to state that the behaviour of particles changes.

! In the Fermi-Dirac statistics, there is a "competition" in populating a state: if the state is occupied by a particle, another particle cannot occupy it. There is no such competition in the Bose-Einstein statistics: a particle can occupy a certain state regardless of whether it is occupied by other particles or it is free. Naturally, if the "competition" in the Fermi-Dirac statistics is not significant, its results must be close to those of the Bose-Einstein statistics. This is the case when the number of particles competing for a state is small, i.e. if the average number of particles per state is not large. In this case, the Fermi-Dirac and Bose-Einstein distributions coincide and are reduced to the Maxwell-Boltzmann distribution.

Sec. 25. THE FERMI-DIRAC DISTRIBUTION

The Fermi-Dirac distribution is derived by using combinatorial methods by direct calculation of the number of states for a fixed number of particles and total energy. The limiting transition to the Gibbs distribution is analyzed.

CALCULATION OF THE NUMBER OF STATES. Quantum-mechanical states of a particle are characterized by a discrete set of possible values of energy, viz. the energy levels. Each energy level includes a number of states with the same energy but differing in respect of some other properties. The problem consists in determining different ways in which the particles can occupy available states in accordance with "regulations" imposed by the model.

For the clarity of representation, we shall visualize various energy levels as large boxes, while different states having the same energy as small cages inside these boxes (Fig. 53). The number of large boxes is equal to the number of energy levels, and the number of small cages in the i th large box is denoted by g_i . Generally speaking, the number of small cages in different large boxes is different. The particles in such a model are represented as balls that must be placed in small cages. In the Bose-Einstein model, each small cage can contain any number of balls, while in the Fermi-Dirac model, there can be no two balls in one cage. The balls are indistinguishable. Let us denote the number of balls by n and calculate the number of possible arrangements of the balls for the Fermi-Dirac model.

Each large box may contain n_i particles, where $n_i \leq g_i$. The total number of particles in all the boxes is $n = \sum n_i$. First of all, let us find the number of ways in which n_i indistinguishable objects can be distributed among g_i places. This problem has already been solved. Its solution is given by formula (5.4) which has the following form for the case under consideration:

$$\Gamma_i = g_i! / [n_i! (g_i - n_i)!]. \quad (25.1)$$

The microscopic states in each of the large boxes are independent, and it is not important which of n particles are there in a particular box. Hence the total number of states in the set of all the large boxes is equal to the product of the number of microscopic states in individual large boxes:

$$\Gamma = \prod_i \Gamma_i = \prod_i \frac{g_i!}{n_i! (g_i - n_i)!}, \quad (25.2)$$

where the symbol $\prod$ denotes the product:

$$\prod_{i=1}^m a_i = a_1 a_2 \dots a_m. \quad (25.3)$$

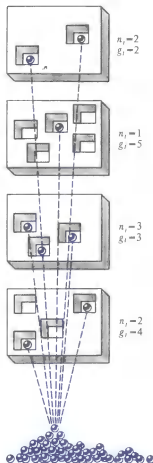


Fig. 53. The model of distribution of particles over energies

We consider that i in the product (25.2) takes into account all the large boxes.

Formula (25.2) is the solution of the problem of calculating the number of microscopic states for the Fermi-Dirac model.

THE FERMI-DIRAC DISTRIBUTION. An equilibrium state is determined by the requirement that the number of states Γ is maximum. This number depends on n_i , i.e. on the energy distribution of particles. In calculations, it is more convenient to use $\ln \Gamma$ instead of Γ . If the numbers n_i were independent, the condition of extremum for $\ln \Gamma$ would have the form

$$\delta \ln \Gamma = \sum_i \frac{\partial \ln \Gamma}{\partial n_i} \delta n_i = 0 \quad (25.4)$$

and would be reduced to the equation $(\partial \ln \Gamma / \partial n_i) = 0$ owing to the independence of n_i . However, n_i are actually not independent quantities. They are related through the condition that the total number of particles is constant:

$$\sum n_i = N, \quad (25.5)$$

which means that

$$\delta n = \sum \frac{\partial n}{\partial n_i} \delta n_i = 0 = \sum \delta n_i, \quad (25.6)$$

and the condition that the energy is constant:

$$\sum \varepsilon_i n_i = U, \quad (25.7)$$

which leads to

$$\delta U = \sum \frac{\partial U}{\partial n_i} \delta n_i = \sum \varepsilon_i \delta n_i = 0. \quad (25.8)$$

Conditions (25.4), (25.6), and (25.8) must be satisfied simultaneously, and the quantities n_i in each of them cannot be considered to be independent. Let us multiply (25.6) and (25.8) by indeterminate constants $-\alpha$ and $-\beta$ respectively and sum the results:

$$(\delta \ln \Gamma - \beta \delta U - \alpha \delta n) = \sum_i \left[\frac{\partial \ln \Gamma}{\partial n_i} - \beta \varepsilon_i - \alpha \right] \delta n_i = 0. \quad (25.9)$$

The constants β and α in this equation account for the interdependence of quantities n_i . Consequently, all n_i 's in

(25.9) can be considered to be independent. This means that the multipliers of δn_i 's must be equal to zero, and hence the condition for extremum is written in the form

$$\frac{\partial \ln \Gamma}{\partial n_i} - \beta \epsilon_i - \alpha = 0. \quad (25.10)$$

The above method of finding the extremum is called the method of Lagrange multipliers. Since the values of n_i 's are very large, Stirling's formula (5.13) is used for calculating $\ln \Gamma$, which gives

$$\frac{\partial \ln \Gamma}{\partial n_i} = \ln \left(\frac{g_i}{n_i} - 1 \right). \quad (25.11)$$

Consequently, Eq. (25.10) assumes the form

$$\ln \left(\frac{g_i}{n_i} - 1 \right) - \beta \epsilon_i - \alpha = 0. \quad (25.12)$$

Taking antilogarithms, we get

$$\frac{n_i}{g_i} = \frac{1}{\exp(\alpha + \beta \epsilon_i) + 1}, \quad (25.13)$$

!

In the Fermi-Dirac statistics, the "competition" among particles in populating the states is extremely intense, since a state occupied by a particle is not accessible to other particles. In a certain sense, it can be said that a particle occupying some state "repels" other particles from this state, as if "keeping" them at a certain distance from its state. The "competition" among particles weakens when the number of states allowed for the particles is much greater than the number of particles.

where n_i/g_i is the number of particles per quantum-mechanical state with energy ϵ_i . This formula is called the Fermi-Dirac distribution.

LIMIT TRANSITION TO THE MAXWELL-BOLTZMANN DISTRIBUTION. If the values of n_i/g_i are very small, the exponent in the denominator on the right-hand side of (25.13) is considerably greater than unity. Hence, we can neglect unity in the denominator and write the distribution in the following form:

$$n_i = A g_i e^{-\beta \epsilon_i}, \quad (25.14)$$

where $A = e^{-\alpha}$. If in this equation we go over to the continuous energy spectrum, taking into account formulas (7.7) and (8.1), we obtain exponential distribution (8.2) of the Maxwell-Boltzmann classical statistics. Thus, we have proved that the formulas of the Fermi-Dirac statistics become the formulas of the Maxwell-Boltzmann statistics when the average number of particles per quantum state is small.

DETERMINATION OF PARAMETER β . The meaning of the parameter β can be clarified by using the limiting transition. Since we know that $\beta = 1/(kT)$ in (25.14), this parameter will have the same value in (25.13) as well. The meaning of the parameter β can also be elucidated directly from formula (25.13) without resorting to the limiting transition. For this purpose, we find the expression for entropy and compare it with the expression $dS = dU/T$ for the entropy at constant volume. This also gives $\beta = 1/(kT)$. We shall not give this derivation here.

DETERMINATION OF PARAMETER α . The parameter α is determined by the normalization to the total number of particles, which expresses the condition of conservation of the number of particles:

$$n = \sum_i n_i = \sum_i \frac{g_i}{\exp[\alpha + \beta \epsilon_i] + 1}. \quad (25.15)$$

Sec. 26. THE BOSE-EINSTEIN DISTRIBUTION

The Bose-Einstein distribution is derived by combinatorial methods, by direct calculation of the number of states at a fixed number of particles and total energy. The possibility of limit transition to the Maxwell-Boltzmann distribution is indicated.

CALCULATION OF THE NUMBER OF STATES. Each quantum-mechanical state in the Bose-Einstein model may contain an arbitrary number of indistinguishable particles. We shall use the same model of large boxes, small cages, and balls as in Sec. 25. At first, we assume that all g_i small cages and n_i balls are distinguishable. We shall distribute the balls over small cages as follows: we assign a number to a cage and enumerate all the balls contained in it; then we number the next cage and enumerate the balls contained in this cage, and so on. If a cage contains no balls, its number is followed by the number of the next cage. We denote the small cages in a large box by the symbols $i_1, i_2, \dots, i_{g_i}$ and the balls by the symbols $j_1, j_2, \dots, j_{n_i}$. Thus, a particular filling of a large box has, for example, the following form:

$$i_k j_l j_r j_{r'} \dots i_{k'} i_{k''} j_m i_q j_{k'''} \dots \quad (26.1)$$

The sequence represented by this formula has the following meaning. The i_k th small cage contains the balls with numbers $j_l, j_r, j_{r'}, \dots$, the $i_{k'}$ th cage is empty, the $i_{k''}$ th cage contains only one ball numbered j_m , the i_q th cage contains the balls $j_{k'''}$, etc. Let us take a specific cage as the first in (26.1). Then the number of possible different ways of filling is equal to the number of permutations of all the elements following this

first cage. The number of these elements is equal to $g_i - 1 + n_i$, while the number of permutations is $(g_i - 1 + n_i)!$. Since such a number of permutations is possible in each case when a specific cage occupies the first place, the number of different combinations for all g_i cages is equal to $g_i(g_i - 1 + n_i)!$. We carried out this calculation under the assumption that the balls are distinguishable and the order in which the cages are arranged is significant. But since only the number of balls in a specific cage is important and the order in which the cages are arranged is immaterial, we must divide the number of combinations obtained above by $g_i!n_i!$. Consequently, we obtain the following expression for the total number of different microscopic states of n_i particles in g_i quantum-mechanical states belonging to the energy ε_i :

$$\Gamma_i = [g_i(g_i - 1 + n_i)!] / (g_i!n_i!). \quad (26.2)$$

The total number of microscopic states is equal to

$$\Gamma = \prod_i \Gamma_i = \prod_i \frac{g_i(g_i - 1 + n_i)!}{g_i!n_i!} \quad (26.3)$$

THE BOSE-EINSTEIN DISTRIBUTION. All subsequent considerations and calculations are exactly the same as in the case of the Fermi-Dirac distribution, starting from formula (25.2). The formula equivalent to (25.10) has the same form but with $\ln \Gamma$ obtained from (26.3). Instead of (25.12) and (25.13), we find

$$\ln \left(\frac{g_i}{n_i} + 1 \right) - \beta \varepsilon_i - \alpha = 0, \quad (26.4)$$

and

$$\frac{n_i}{g_i} = \frac{1}{\exp(\alpha + \beta \varepsilon_i) - 1} \quad (26.5)$$

respectively.

This formula is called the Bose-Einstein distribution. As in the case of the Fermi-Dirac distribution, this formula is transformed to the Maxwell-Boltzmann distribution (25.14) when the average number of particles per quantum-mechanical state is sufficiently small.

Sec. 27. THE ELECTRON GAS

The basic properties of the electron gas are described. The properties of the electron gas in different conditions are analyzed on the basis of the Fermi-Dirac distribution. The Fermi energy and the characteristic temperature are calculated. The internal energy of the electron gas and heat capacity corresponding to it are considered.

FREE ELECTRONS IN METALS. Electrical conductivity of metals is due to the presence of "free" electrons in them, i.e. the electrons that do not belong to a particular atom. These electrons are sort of collectivized and belong to all the atoms of the metal. Consequently, we cannot state that these electrons are free in the same sense as the particles in an ideal gas or the molecules in not very dense gases. The electrons interact, though very weakly, with the totality of all the atoms. The electron energy levels are arranged very close to each other in view of the large number of atoms with which they interact and the large region of space where they move (the entire volume of the metal). Their momenta may also have different directions at each point of space. All this resembles the motion of molecules in a gas, and the totality of such electrons is called the electron gas. On the average, their charge is compensated by the opposite charge of the metal atoms whose electrons form the electron gas. The metal is electrically neutral on the whole.

DETERMINATION OF PARAMETER α FOR THE ELECTRON GAS. In order to obtain the formula (25.15) for the electron gas, we proceed in the same way as in Sec. 8 [see (8.1)]. The volume of an elementary cell of the phase volume, where only one particle can exist, is equal to $(2\pi\hbar)^3$. Therefore, the number of quantum-mechanical states in the element $\Delta p_{xi}\Delta p_{yi}\Delta p_{zi}\Delta x_i\Delta y_i\Delta z_i$ of the phase volume is equal to

$$g_i = \frac{g}{(2\pi\hbar)^3} \Delta p_{xi}\Delta p_{yi}\Delta p_{zi}\Delta x_i\Delta y_i\Delta z_i, \quad (27.1)$$

where g takes into account the internal degrees of freedom of the particle. An electron has a spin which can take on one of two values. Hence $g = 2$ for electrons. However, for the sake of generality of the formulas being derived, we shall retain g without specifying its numerical value.

Substituting (27.1) into (25.15), we get

$$n = \frac{g}{(2\pi\hbar)^3} \sum_i \frac{\Delta p_{xi}\Delta p_{yi}\Delta p_{zi}\Delta x_i\Delta y_i\Delta z_i}{\exp(\alpha + \beta \epsilon_i) + 1}. \quad (27.2)$$

On account of smallness of an elementary cell of the phase volume and considering that the energy of a free electron is expressed in terms of its momentum through the formula $\epsilon_i = p_i^2 / (2m_e)$, we go over in (27.2) from summation to

integration:

$$n = \frac{g}{(2\pi\hbar)^3} \int_V dx dy dz \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{dp_x dp_y dp_z}{\exp[\alpha + \beta p^2/(2m_e)] + 1}, \quad (27.3)$$

where V is the volume occupied by the gas. Integration over spatial coordinates gives the volume V , while in integrating over momenta we can go over to spherical coordinates in the momentum space. Taking into account the spherical symmetry, we can put $dp_x dp_y dp_z = 4\pi p^2 dp$. This gives

$$n = \frac{4\pi g V}{(2\pi\hbar)^3} \int_0^{\infty} \frac{p^2 dp}{\exp[\alpha + p^2/(2m_e kT)] + 1}, \quad (27.4)$$

where $\beta = 1/(kT)$. Making in this equation the substitution of variables $\xi = p^2/(2m_e kT)$, we obtain

$$n = \frac{4\pi g V}{(2\pi\hbar)^3} \frac{(2m_e kT)^{3/2}}{2} \int_0^{\infty} \frac{\sqrt{\xi} d\xi}{e^{\alpha + \xi} + 1}. \quad (27.5)$$

By using the notation

$$F_{(+)}(\alpha) = \frac{2}{\sqrt{\pi}} \int_0^{\infty} \frac{\sqrt{\xi} d\xi}{e^{\alpha + \xi} + 1} \quad (27.6)$$

we write (27.5) in the form

$$n = g V [m_e kT / (2\pi\hbar^2)]^{3/2} F_{(+)}(\alpha). \quad (27.7)$$

The integral $F_{(+)}(\alpha)$ is called the **Fermi integral**. This integral cannot be evaluated analytically but can be represented in the form of a series. Without going into details of mathematical calculations, we just give the result. For negative values of α , i.e. for $-\alpha > 0$, and taking into account the principal term of the expansion, we obtain the following formula in the first approximation:

$$F_{(+)}(\alpha) = 4(-\alpha)^{3/2} / (3\sqrt{\pi}). \quad (27.8)$$

Hence, formula (27.7) assumes the form

$$n = \frac{4gV}{3\sqrt{\pi}} \left(-\frac{m_e kT\alpha}{2\pi\hbar^2} \right)^{3/2}. \quad (27.9)$$

Thus we have expressed α in terms of other quantities appearing in (27.9):

$$\alpha = - \frac{2\pi\hbar^2}{m_e kT} \left(\frac{3n\sqrt{\pi}}{4gV} \right)^{2/3}, \quad (27.10)$$

where m_e is the electron mass.

The number of free electrons per atom in a metal can be different, but usually it is close to one electron per atom. Hence we can assume that the number of free electrons is equal to the number of atoms. If the density of a metal is ρ and the mass of an atom is m_a , then $n = \rho V/m_a$, and equation (27.10) assumes the form

$$\alpha = - \frac{2\pi\hbar^2}{m_e kT} \left(\frac{3\rho\sqrt{\pi}}{4gm_a} \right)^{2/3}. \quad (27.11)$$

Let us estimate the numerical value of α . For example, for copper $\rho = 8.8 \times 10^3 \text{ kg/m}^3$, $m_a = (M/N_A) = 0.063/(6.02 \times 10^{23}) \text{ kg}$, where M is the molar mass. Substituting these values and $T = 300 \text{ K}$ into (27.11), we find $\alpha = -271$. This means that the value of $\exp[\alpha + \epsilon/(kT)]$ in the denominator of the Fermi-Dirac distribution is small up to very high electron energies. In the case under consideration, we have $\exp[\alpha + \epsilon/(kT)] \ll e^{-6}$ up to the energy $\epsilon \approx 265 \text{ kT}$, i.e. the exponential term in the denominator of the distribution can be ignored. Since $kT = 1.38 \times 10^{-23} \times 300 \text{ J} = 2.59 \times 10^{-2} \text{ eV}$ for $T = 300 \text{ K}$, this term can be neglected up to the electron energy of about 6.86 eV . This energy is quite large, and only a few electrons in a metal may have such an energy or higher. Therefore, for an overwhelming majority of electrons the exponential term in the denominator of the Fermi-Dirac distribution can be put equal to zero.

ANALYSIS OF THE FERMI-DIRAC DISTRIBUTION. Let us introduce a new quantity μ which is connected with α through the relation

$$\mu = -\alpha kT. \quad (27.12)$$

Then the distribution (25.13) can be written in the form

$$\frac{n_i}{g_i} = \frac{1}{\exp[(\epsilon_i - \mu)/(kT)] + 1}. \quad (27.13)$$

! The Fermi energy of metals can be clearly interpreted as the maximum energy of electrons at 0 K. For insulators and semiconductors the Fermi energy lies in the forbidden energy band for electrons and hence, in principle, no electron can have such an energy. The Fermi energy can be defined as the energy for which the Fermi-Dirac distribution is equal to 1/2. This definition is also valid for metals.

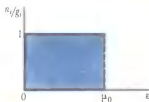


Fig. 54. The Fermi-Dirac distribution for $T = 0$ K.

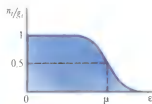


Fig. 55. The Fermi-Dirac distribution for $0 \text{ K} < T < T_F$.

For $\varepsilon_i < \mu$, $T \rightarrow 0$ K, we have $\exp[(\varepsilon_i - \mu)/(kT)] \rightarrow 0$, and hence $(n_i/g_i) \rightarrow 1$, i.e. each quantum-mechanical state with an energy lower than μ contains one particle. For $\varepsilon_i > \mu$, $T \rightarrow 0$ K, we have $\exp[(\varepsilon_i - \mu)/(kT)] \rightarrow \infty$ and hence $(n_i/g_i) \rightarrow 0$, i.e. the quantum-mechanical states with an energy $\varepsilon > \mu$ are empty (there is not a single particle in such states). The form of the Fermi-Dirac distribution for $T = 0$ K is shown in Fig. 54. Such a form of the distribution is necessitated by two requirements. Firstly, the total energy must be minimum and secondly, the Pauli exclusion principle must be satisfied. For this reason, electrons start to populate quantum-mechanical states from the lowest energy level and occupy the quantum states successively, each being occupied by one electron. After all the electrons are exhausted, the filling process is completed. The last electron occupies the level corresponding to the maximum energy. This level is called the Fermi level and the energy corresponding to this level is called the Fermi energy. Such a graphical definition is applicable only to free electrons in a metal. In the general case, this definition is not exact. For example, in a dielectric the Fermi energy corresponds approximately to the middle of the forbidden band, and it is known beforehand that there are no electrons that have such an energy. Thus, a more general definition will be: the Fermi energy is the energy for which the Fermi-Dirac distribution (25.13) assumes the value $1/2$. It follows from (27.13) that μ is the Fermi energy.

When $T > 0$ K, the Fermi-Dirac distribution is blurred in the vicinity of the Fermi level (Fig. 55). This blurring is caused by the interaction between the electrons and thermal motion of atoms. Since the mean energy of thermal motion is of the order of kT , the region of blurring of the electron energy in the vicinity of the Fermi level has also the same order.

THE FERMI ENERGY. In accordance with (27.12), the determination of the Fermi energy is reduced to the determination of the parameter α . To a first approximation, it is equal to $\mu_0 = -\alpha kT$, where α is given by (27.10) for $g = 2$:

$$\mu_0 = \frac{\pi^2 \hbar^2}{2m_e} \left(\frac{3n}{\pi V} \right)^{2/3}, \quad (27.14)$$

i.e. it is independent of temperature. However, it follows from the general definition of α that the Fermi energy depends on temperature.

This dependence is included in the terms of the expansion for α , which follow the term that was taken into account (27.10). Calculations lead to the formula

$$\mu = \mu_0 \left[1 - \frac{\pi^2}{12} \left(\frac{kT}{\mu_0} \right) + \dots \right], \quad (27.15)$$

CHARACTERISTIC TEMPERATURE. The temperature dependence of the Fermi energy becomes significant when the second term in the brackets on the right-hand side of (27.15) approaches unity, i.e. at a temperature

$$T_F = \mu_0/k, \quad (27.16)$$

which is called the characteristic, or Fermi temperature. Taking into account (27.14), we can represent formula (27.16) as follows:

$$T_F = \frac{\pi^2 \hbar^2}{2m_e k} \left(\frac{3n}{\pi V} \right)^{2/3}. \quad (27.17)$$

Let us estimate the order of magnitude of this temperature, for example, for copper. As the value of α for copper has already been calculated at $T = 300$ K by using formula (27.17), we obtain $T_F = 8.13 \times 10^4$ K from (27.10). This value is much higher than the melting point for copper. For other metals, the characteristic temperatures are also of the order of 10^4 , while melting points are of the order of 10^3 . Hence, the condition $T \ll T_F$ is observed for most of metals in the solid state; the Fermi energy for these metals can be taken equal to μ_0 , and the distribution of the electron gas in them differs only slightly from the Fermi-Dirac distribution at 0 K. Such a gas is called a strongly degenerate Fermi gas. The Fermi temperature is characteristic of a degenerate gas and is therefore called the characteristic temperature.

MOMENTUM DISTRIBUTION OF ELECTRONS. According to (27.13) and (27.4), the number dn of electrons whose momenta lie between p and $p + dp$ is equal to

$$dn_p = \frac{8\pi V}{(2\pi\hbar)^3} \frac{p^2 dp}{\exp[(\epsilon - \mu)/(kT)] + 1}. \quad (27.18)$$

In the case of degeneracy, the exponential term in the denominator can be put equal to zero.

VELOCITY DISTRIBUTION OF ELECTRONS. Putting $p = mv$ in (27.18), we obtain

?

1. Under which circumstances can we represent free electrons in a metal as an electron gas?
2. How does the Fermi energy depend on the uniform pressure?
3. What is the order of magnitude of the characteristic temperature for most metals? What consequences follow from this?
4. Under which conditions is the electron heat capacity of metals significant?

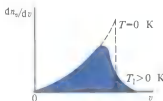


Fig. 56. The velocity distribution for electrons for $T > 0$ and $T = 0$

$$dn_v = \frac{m_e^3 V}{\pi^2 \hbar^3} \frac{v^2 dv}{\exp[(\epsilon - \mu)/(kT)] + 1}, \quad \epsilon = \frac{m_e v^2}{2}. \quad (27.19)$$

The velocity distribution of electrons is shown in Fig. 56. When $T = 0$ K, no electrons may have velocities higher than those corresponding to the Fermi energy.

ENERGY DISTRIBUTION OF ELECTRONS. Changing from the variable p in (27.18) to the variable $\epsilon = p^2/(2m_e)$, we obtain the formula for the energy distribution of electrons:

$$dn_\epsilon = \frac{V}{2\pi^2} \left(\frac{2m_e}{\hbar^2} \right)^{3/2} \frac{\epsilon^{1/2} d\epsilon}{\exp[\beta(\epsilon - \mu)] + 1}, \quad \beta = \frac{1}{kT}. \quad (27.20)$$

The form of this distribution is shown in Fig. 57.

MEAN ELECTRON ENERGY. For $T = 0$ K, the mean energy is

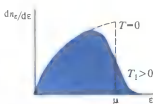


Fig. 57. The energy distribution for electrons for $T_1 > 0$

$$\langle \epsilon \rangle = \frac{\int_0^{\mu_0} \epsilon dn_\epsilon}{\int_0^{\mu_0} dn_\epsilon} = \frac{3}{5} \mu_0, \quad (27.21)$$

where we have taken into account the fact that only the electrons with energies $\epsilon \leq \mu_0$ take part in the distribution at $T = 0$ K. Consequently, we integrate between 0 and μ_0 . Besides, the denominator in (27.20) is equal to unity in this case, and the energy distribution assumes the form

$$dn_\epsilon = \frac{V}{2\pi^2} \left(\frac{2m_e}{\hbar^2} \right)^{3/2} \epsilon^{1/2} d\epsilon. \quad (27.22)$$

If the temperature differs from zero, we must use formula (27.20) for calculating $\langle \epsilon \rangle$ with the value of μ given by (27.15). As a result of calculations, we get

$$\langle \epsilon \rangle = \frac{3}{5} \mu_0 \left[1 + \frac{5}{12} \pi^2 \left(\frac{kT}{\mu_0} \right)^2 + \dots \right]. \quad (27.23)$$

INTERNAL ENERGY AND HEAT CAPACITY. According to (27.23), the internal energy U of the electron gas is equal to

$$U = n \langle \epsilon \rangle = \frac{3}{5} n \mu_0 + \frac{1}{4} \frac{\pi^2 k^2 n}{\mu_0} T^2, \quad (27.24)$$

where n is the total number of electrons in a metal. If it is equal to the Avogadro constant N_A , then U is the internal energy of a mole of electrons. The molar heat capacity C_V at constant volume can be expressed through (27.24) as follows:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{\pi^2}{2} \frac{kT}{\mu_0} kN_A = \frac{\pi^2}{2} \frac{kT}{\mu_0} R. \quad (27.25)$$

In accordance with the Dulong and Petit law, $C_V = 3R$, which is immeasurably greater than (27.25) since $kT \ll \mu_0$ under normal conditions. This means that electronic heat capacity of metals is negligibly small. Physically, this is due to the fact that only a small part of the total number of electrons, viz. the electrons located near the Fermi level, take part in the thermal motion at normal temperature. Consequently, the degenerate electron gas does not behave as an ordinary gas. In particular, its contribution to heat capacity cannot be calculated simply by applying the principle of equipartition of energy to it.

The statement that the value of the electron heat capacity is insignificant is valid only for high temperatures. At sufficiently low temperatures, the electron heat capacity exceeds the heat capacity determined by thermal vibrations of lattice atoms of a solid, since the latter decreases in proportion to T^3 and becomes negligibly small at very low temperatures (see Sec. 46).

Example 27.1. Find the number of free electrons in 10 cm^3 of copper and the number of electrons whose energies lie between 7.01 and 7.001 eV at $T = 300 \text{ K}$.

The concentration of free electrons in copper with density ρ is equal to $(\rho/m_e) = [8.9 \times 10^3 \times 6.02 \times 10^{23}/0.0636] \text{ m}^{-3} = 8.4 \times 10^{28} \text{ m}^{-3}$. There are $8.4 \times 10^{28} \times 10^{-5} = 8.4 \times 10^{23}$ electrons in 10 cm^3 of copper. The Fermi energy is equal to $\mu_0 = \alpha kT = 271 \times 1.38 \times 10^{-23} \times 300 \text{ J} = 7.01 \text{ eV}$. Hence we must find the number of electrons in the region where the Fermi distribution changes abruptly and take due care while making the calculations. Let us pay attention to the fact that $kT = 1.38 \times 10^{-23} \times 300 \text{ J} = 4.14 \times 10^{-21} \text{ J} = 2.59 \times 10^{-2} \text{ eV}$. This means that the exponential term varies from 1 to $\exp(1/2.59) = 0.68$ over the interval 0.01 eV from the Fermi energy, which makes it impossible to replace the differential by a finite value of $de = 0.01 \text{ eV}$ for such or larger intervals. In this case, it is necessary to evaluate the integral more precisely. However, the exponential varies insignificantly over the interval of 0.001 eV, and we can replace the differential by a finite

quantity $\varepsilon = 0.001$ eV. Then formula (27.20) gives

$$\begin{aligned} dn_{\varepsilon} &= \frac{10^{-5}}{2(3.14)^2} \\ &\times \frac{(2 \times 9.1 \times 10^{-31})^{3/2} (7.01 \times 1.6 \times 10^{-19})^{1/2} 0.001 \times 1.6 \times 10^{-19}}{(1.05 \times 10^{-34})^3 [\exp 0 + 1]} \\ &= 9 \times 10^{20}. \end{aligned}$$

When $\varepsilon \ll \mu_0$, the exponential term in the denominator can be put equal to zero, and for $\varepsilon \gg \mu_0$ we can neglect unity in comparison with the exponential term.

Example 27.2. Find the maximum velocity of free electrons in copper at $T = 0$ K.

For $T = 0$ K, the gas is completely degenerate, and hence all the states with energies from zero to the Fermi level are filled. The maximum velocity $v_{\max}$ in this case is connected with μ_0 through the relation $m_e v_{\max}^2 = 2\mu_0$, i.e. $v_{\max} = (2\mu_0/m_e)^{1/2}$. From (27.19) we get

$$n = \int_{v=0}^{v=v_{\max}} dn_v = \frac{m_e^3 V}{\pi^2 \hbar^3} \int_0^{v_{\max}} v^2 dv = \frac{m_e^3 V v_{\max}^3}{3\pi^2 \hbar^3}, \quad (27.26)$$

where n is the total number of free electrons in the volume V . Then

$$v_{\max} = \frac{\hbar \pi^{2/3}}{m_e} \left(\frac{3n}{V} \right)^{1/3} = \frac{\hbar (3\pi^2)^{1/3}}{m_e} \left(\frac{n}{V} \right)^{1/3}. \quad (27.27)$$

For copper we have

$$\begin{aligned} \frac{n}{V} &= \frac{\rho}{m_a} = \frac{\rho N_A}{M} = \left[\frac{8.9 \times 10^3 \times 6.02 \times 10^{23}}{0.0636} \right] \text{m}^{-3} \\ &= 8.4 \times 10^{28} \text{m}^{-3}, \end{aligned}$$

whence

$$\begin{aligned} v_{\max} &= \frac{1.05 \times 10^{-34} (3 \times 3.14 \times 3.14)^{1/3}}{9.11 \times 10^{-31}} (8.4 \times 10^{28})^{1/3} \text{ m/s} \\ &= 157 \times 10^4 \text{ m/s} = 1570 \text{ km/s}. \end{aligned} \quad (27.28)$$

In interpreting this result we must bear in mind that, strictly speaking, the mass of free electrons in a metal is not equal to the mass of free electrons in vacuum. In a more precise theory, the mass of free electrons in a metal is

identified with their effective mass that can considerably differ from the rest mass of electrons. This difference was not taken into account in (27.28).

Sec. 28. THE PHOTON GAS

The Bose-Einstein distribution is applied to photons, whose number need not be constant. Planck's formula and the Stefan-Boltzmann and Wien displacement laws following from it are derived. Basic properties of the black-body radiation are considered.

BLACK-BODY RADIATION. Black-body radiation is the equilibrium radiation that sets in in a closed cavity whose walls are kept at a certain temperature. The radiation inside the cavity is created by photons with energy ε_i and momentum p_i expressed through the following formulas

$$\varepsilon_i = \hbar\omega_i, \quad p_i = \hbar\omega_i/c. \quad (28.1)$$

The aggregate of photons in the cavity is called the photon gas, since in this case the photons can be treated as particles moving without collisions. The photon spin is equal to unity, hence they obey the Bose-Einstein statistics.

DISTRIBUTION OF PHOTONS. Photons in a cavity are continuously generated and annihilated. Consequently, when deriving the energy distribution of photons we do not have any limitation concerning the constant number of photons. The total number of microscopic states of photons is, naturally, given by formula (26.3). However, the condition $\sum \delta n_i = 0$ for the constant number of particles is missing, and hence the term containing α in Eq. (26.4) is also absent. As a result, $\alpha = 0$ in expression (26.5) for the energy distribution of photons, which in this case assumes the form

$$\langle n(\varepsilon_i) \rangle = \frac{n_i}{g_i} = \frac{1}{\exp(\beta\varepsilon_i) - 1}. \quad (28.2)$$

FREQUENCY DISTRIBUTION OF PHOTONS. The calculation of the number of photons in the phase space and all other considerations and calculations are similar to those considered in detail for the Fermi-Dirac distribution applied to the electron gas, the only difference being that we must take distribution (28.2) instead of (27.10). As a result, instead of formula (27.2) for the number dn_p of photons whose momenta lie in the interval $(p, p + dp)$, we get

$$dn_p = \frac{1}{\exp(\beta\varepsilon) - 1} \frac{2}{(2\pi\hbar)^3} V \cdot 4\pi p^2 dp, \quad (28.3)$$

where $\varepsilon = cp$, and the factor 2 in the numerator takes into account two possible transverse polarizations of a photon. It



Max Karl Ernst Ludwig
Planck
(1858-1947)

should be recalled that in the case of electrons this factor took into account two possible orientations of the electron spin.

Going over from momenta p to frequencies $\omega = pc/\hbar$ in (28.3), we obtain

$$dn_{\omega} = \frac{\omega^2 V}{\pi^2 c^3} \frac{1}{\exp(\beta \hbar \omega) - 1} d\omega. \quad (28.4)$$

PLANCK'S FORMULA. The energy of each photon is equal to $\hbar\omega$, hence the spectral density of radiant energy has the form

$$w_{\omega} = \frac{\hbar\omega}{V} \frac{dn_{\omega}}{d\omega} = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{\exp[\hbar\omega/(kT)] - 1}. \quad (28.5)$$

This expression is called Planck's formula. The discovery of this formula by M. Planck and the attempts at its interpretation laid the basis for the development of quantum-mechanical concepts and creation of quantum mechanics.

STEFAN-BOLTZMANN LAW. The total density of radiant energy is given by

$$\begin{aligned} w &= \int_0^{\infty} w_{\omega} d\omega = \frac{\hbar}{\pi^2 c^3} \int_0^{\infty} \frac{\omega^3 d\omega}{\exp[\hbar\omega/(kT)] - 1} \\ &= \frac{\hbar}{\pi^2 c^3} \left(\frac{kT}{\hbar}\right)^4 \int_0^{\infty} \frac{\xi^3 d\xi}{\exp \xi - 1}. \end{aligned} \quad (28.6)$$

Considering that $\int_0^{\infty} \frac{\xi^3 d\xi}{\exp \xi - 1} = \frac{\pi^4}{15}$, we can represent the radiant energy density in the form

$$w = aT^4, \quad (28.7a)$$

where

$$a = k^4 \pi^2 / (15c^3 \hbar) = 7.56 \times 10^{-16} \text{ J} \cdot \text{m}^{-3} \cdot \text{K}^{-4}. \quad (28.7b)$$

It is convenient to use the concept of radiant emittance (emissivity) instead of the equilibrium radiation density. This quantity characterizes the density of radiant flux leaving the

surface in all directions (within the solid angle of 2π). It is equal to the flux per unit area. Radiant emittance is connected with the radiant energy density through the relation

$$M = cw/4 = \sigma T^4, \quad (28.8a)$$

where

$$\sigma = ca/4 = 5.67032 \times 10^{-8} \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-4}. \quad (28.8b)$$

Formula (28.8a) is called the **Stefan-Boltzmann law** and σ the **Stefan-Boltzmann constant**.

WIEN DISPLACEMENT LAW. Formula (28.5) can be used to find the maximum of the spectral density of radiation. The position of the maximum depends on the scale on which it is determined. We can calculate it on the wavelength scale by going over to wavelength $\lambda = 2\pi c/\omega$ and taking into account that

$$w_\omega d\omega = -w_\lambda 2\pi c d\lambda/\lambda^2. \quad (28.9)$$

Consequently, the distribution of the radiant energy density among wavelength has the form

$$w_\lambda \sim \frac{1}{\lambda^5} \frac{1}{\exp[2\pi\hbar c/(kT\lambda)] - 1}, \quad (28.10)$$

where we have omitted the constant factors which are unimportant for further calculations. The maximum radiation density can be found from the condition for the extremum:

$$\partial w_\lambda / \partial \lambda = 0, \quad (28.11)$$

which gives the following expression for determining the wavelength $\lambda_{\max}$ corresponding to the maximum radiation density:

$$5 = xe^x/(e^x - 1), \quad x = 2\pi\hbar c/(kT\lambda_{\max}). \quad (28.12)$$

The solution of this equation is $x = 4.965$. Therefore, $\lambda_{\max}$ is determined from the expression

$$\lambda_{\max} T = 2\pi\hbar c/(kx) = 0.0029 \text{ m} \cdot \text{K}, \quad (28.13)$$

which is called the **Wien displacement law**. As the temperature of the black body increases, the maximum



Fig. 58. The spectrum of the black-body radiation

radiation density in its spectrum is displaced towards smaller wavelengths, i.e. towards higher frequencies. A black-body radiation spectrum is shown in Fig. 58.

Example 28.1. Find the number of photons emitted from the surface of area S in the frequency interval from ω_1 to ω_2 at a temperature T .

In accordance with (28.8) and (28.5), the required number of photons can be expressed as follows:

$$dn = \frac{c}{4} \int_{\omega_1}^{\omega_2} \frac{w_{\omega}}{\hbar\omega} d\omega = \frac{1}{4\pi^2 c^2} \int_{\omega_1}^{\omega_2} \frac{\omega^2 d\omega}{\exp[\hbar\omega/(kT)] - 1}.$$

This formula can sometimes be simplified if we deal with the visible part of the spectrum. For the middle of the visible spectral region, $\hbar\omega \simeq 2 \text{ eV}$. For $T = 6000 \text{ K}$ we have $kT = 1.38 \times 10^{-23} \times 10^3 \times 6 \text{ J} = 8.28 \times 10^{-20} \text{ J} = 0.518 \text{ eV}$; $\hbar\omega/(kT) = 3.45$; $\exp[\hbar\omega/(kT)] \simeq 31.5$, and hence we can neglect unity in the denominator. For $T = 6000 \text{ K}$ the formula is simplified if the frequency interval lies in the visible region of the spectrum, and we have

$$n = \frac{1}{4\pi^2 c^2} \int_{\omega_1}^{\omega_2} \exp[-\hbar\omega/(kT)] \omega^2 d\omega.$$

This integral can be easily taken by parts. In general, when we have a complicated integral, it is always useful to estimate the numerical values of various terms in the integrand before trying to evaluate it in the general form. As a result of this estimation the calculations are considerably simplified and the integral that cannot be expressed analytically can be reduced to a comparatively simple analytic expression.

Example 28.2. Boltzmann's constant k and Planck's constant $\hbar$ can be determined by measuring the spectrum of the black-body radiation. The experimentally obtained power of the black-body radiation from a surface of area $S = 1 \text{ m}^2$ to a half-space is $M = 904.48 \text{ kW}$ at $T = 2000 \text{ K}$. The maximum spectral radiation density in this case corresponds to $\lambda_{\max} = 1.451 \times 10^{-6} \text{ m}$. Find the values of the constants k and $\hbar$.

Taking into account (28.7), and combining two equations, (28.13) and (28.8a), for two unknowns k and $\hbar$, we obtain

$$k = \frac{2\pi ch}{4.965\lambda_{\max} T}, \quad (28.14)$$

$$k^4 = \frac{60c^2 M h^3}{\pi^2 T^4}. \quad (28.15)$$

These equations can be easily solved:

$$k = \frac{(4.965)^3 \times 15}{2\pi^5 c} \frac{\lambda_{\max}^3 M}{T}, \quad (28.16)$$

$$h = \frac{(4.965)^4 \times 15}{4\pi^6 c^2} \lambda_{\max}^4 M. \quad (28.17)$$

Substituting the results obtained in experiment, we find

$$\begin{aligned} k &= \frac{(4.965)^3 \times 15 (1.451 \times 10^{-6})^3 \times 904.48 \times 10^3}{2(3.1416)^5 (3 \times 10^8) \times 10^3} \text{ J/K} \\ &= 1.38 \times 10^{-23} \text{ J/K}, \\ h &= \frac{(4.965)^4 \times 15 (1.451 \cdot 10^{-6})^4 \times 904.48 \times 10^3}{4(3.1416)^6 (3 \times 10^8)^2} \text{ J} \cdot \text{s} \\ &= 1.055 \times 10^{-34} \text{ J} \cdot \text{s}. \end{aligned}$$

PROBLEMS

- 3.1. Find the Fermi energy for silver assuming that $\rho = 10.5 \times 10^3 \text{ kg/m}^3$ and $M_s = 107.9$.
- 3.2. Find the total number of electrons in 1 g of silver at $T = 100 \text{ K}$ and the number of electrons whose energies lie between 2.0 and 2.1 eV. Use the parameters for silver given in Exercise 3.1.
- 3.3. Calculate the number of photons in a radiation cavity with volume $V = 1 \text{ m}^3$ and temperature $T = 3500 \text{ K}$, emitting frequencies from $\omega = 3.24 \times 10^{15} \text{ s}^{-1}$ to $\omega + d\omega = 3.27 \times 10^{15} \text{ s}^{-1}$.
- 3.4. Find the number of photons having frequencies between $\omega = 2.16 \times 10^{15} \text{ s}^{-1}$ and $\omega + d\omega = 2.18 \times 10^{15} \text{ s}^{-1}$ in a cavity of volume 1 m^3 at $T = 4000 \text{ K}$. Find the total energy of photons.
- 3.5. Find the number of free electrons in a substance with $\mu_0 = 9.34 \text{ eV}$, whose energies lie between 9.20 and 9.27 eV, contained in the volume 10^{-4} m^3 at $T = 400 \text{ K}$.
- 3.6. Find the wavelength corresponding to the maximum of the energy density of a black-body radiation at $T = 4000 \text{ K}$.
- 3.7. Find the temperature interval for which the maximum of the spectral density of black-body radiation, calculated on the wavelength scale corresponds to the visible spectral interval between $3.9 \times 10^{-7} \text{ m}$ and $7.8 \times 10^{-6} \text{ m}$.

- 3.8. The maximum of the spectral density of solar radiation measured on the wavelength scale corresponds to $\lambda_{\max} = 4.7 \times 10^{-6}$ m. Find the temperature of the surface of the Sun assuming that it emits as a black body.
- 3.9. Find the number of photons in a 1 mm^3 cavity containing black-body radiation at $T = 500$ K.
- 3.10. Find the maximum velocity of free electrons in silver at $T = 0$ K. Use the parameters for silver given in Exercise 3.1.
- 3.11. Find the degeneracy temperature for the electron gas in silver. Use the parameters for silver given in Exercise 3.1.

ANSWERS

3.1. $\mu_0 = 8.8 \cdot 10^{-19}$ J = 5.5 eV. 3.2. $n = 5.6 \cdot 10^{21}$; $dn = 0.9 \cdot 10^{20}$. 3.3. $dn = 5.3 \cdot 10^{14}$. 3.4. $dn = 6 \cdot 10^{15}$; $dW = 1.36 \cdot 10^{-3}$ J. 3.5. $dn = 2 \cdot 10^{25}$. 3.6. $3.053 \cdot 10^{-6}$ m. 3.7. $3720 \text{ K} < T < 7430 \text{ K}$. 3.8. $T = 6170 \text{ K}$. 3.9. $n = 2.55 \cdot 10^6$. 3.10. $v_{\max} = 139 \cdot 10^4 \text{ m/s} = 1390 \text{ km/s}$. 3.11. $6.5 \cdot 10^4 \text{ K}$.



Gases with Intermolecular Interaction and Liquids

Basic physical factor: the forces of interaction between molecules are attractive at large distances and repulsive at short distances.

Basic criterion for determining the result of interaction: the relation between the mean energy of interaction and the mean kinetic energy of molecules.

Sec. 29. FORCES OF INTERACTION

The main types of bonds between molecules are considered. It is noted that the structure of liquids is intermediate between the structure of gases and solids. Van der Waals forces and intermolecular potential are defined. The criterion for the formation of liquid state from gaseous state is analyzed.

BONDING FORCES IN MOLECULES. The electrons in an atom are kept near the nucleus by the Coulomb forces of attraction between unlike charges. Atom as a whole is electrically neutral. Molecules consist of atoms. The forces binding atoms in a molecule are electrical by nature, but they appear in a more complicated way. There are two main types of atomic bonds in a molecule.

IONIC BOND. The forces binding different electrons in an atom to the atom as a whole are different and depend on the atomic structure. The structure of atoms and the laws of motion of electrons in them are studied in quantum mechanics. Here, all we need to know is that one or more electrons are bound very weakly to the atom as a whole. These electrons can be easily detached from the atom, as a result of which a positively charged ion appears.

On the contrary, all the electrons are tightly bound to the atom in some other cases. Moreover, under favourable conditions an atom readily captures an electron or even two electrons and becomes a negatively charged ion. In the process of formation of a molecule, such atoms are converted into ions with a negative charge. The Coulomb forces of attraction acting between unlike ions facilitate the formation of the molecule. A molecule of sodium chloride is an example

of such type of molecules. The structure of this molecule can be represented in the ionic form as Na^+Cl^- , i.e. Na^+ is a positive ion and Cl^- a negative ion. Many other molecules also owe their existence to the ionic bond.

The potential energy of attraction between the Na^+ and Cl^- ions is given by

$$U(r) = -e^2/(4\pi\epsilon_0 r_0), \quad (29.1)$$

where r_0 is the (equilibrium) distance between the ions. Besides this energy, there is a positive energy associated with the repulsive forces which come into play as the ions approach each other at a short distance, since they cannot penetrate into one another. These forces are strong only at small distances between the ions and rapidly decrease with increasing distance. Their contribution to the total energy of interaction between the ions is small and does not exceed $\sim 10\%$ of its total magnitude. Hence, with the accuracy sufficient for an order-of-magnitude estimate, we can obtain from (29.1) the following expression for the energy of dissociation of the NaCl molecule:

$$\Delta E = e^2/(4\pi\epsilon_0 r_0). \quad (29.2)$$

For the gaseous state, the measurements give $r_0 = 2.5 \times 10^{-10}$ m. Considering that $1/(4\pi\epsilon_0) = 9 \times 10^9$ m/F, and $e = 1.6 \times 10^{-19}$ C, formula (29.2) yields $\Delta E \simeq 9 \times 10^{-19}$ J, which coincides with the experimental value to within 5%. Similarly, we can obtain sufficiently good results for other molecules with the ionic bond by using very simple methods.

From a physical point of view, the ionic bond is characterized by a complete exchange of the charge (electron) between ions. A partial exchange leads to the appearance of a covalent bond.

COVALENT BOND. Obviously, the ionic bond cannot explain the existence of molecules consisting of two identical atoms, such as H_2 , O_2 , N_2 , etc., since the two atoms forming a molecule are equivalent, and there is no ground for one of them to become a positive ion and for the other, a negative ion. The bond between atoms in such molecules is called the covalent bond.

A complete understanding of the covalent bond can be gained only in the framework of quantum mechanics, but the physical significance of the problem can be graphically explained even by using the classical concepts.

Two positive charges repel each other with the Coulomb forces





Fig. 59. The mechanism of the covalent bond formation



The forces of attraction acting on the positive charges from the negative charge are four times stronger than the repulsive forces acting between the positive charges. As a result, the positive charges are acted upon by the force tending to bring them closer, i.e. the force of attraction:



The forces exerted on the negative charge by the positive charges are mutually balanced. This is the essence of the process of the formation of the covalent bond. However, a static equilibrium of this type is impossible. Quantum mechanics explains how the motion of electrons appears, in which some electrons on the average move most of time between the positively charged nuclei, i.e. these electrons effectively form a negative charge between the nuclei (Fig. 59). Usually, we deal with two electrons whose motion is collectivized so that we cannot say to which of the atoms forming the molecule they belong. For this reason, the bond appearing in this case is called covalent.

INTERMOLECULAR FORCES IN SOLIDS. Solid state is formed when the binding energy of molecules is considerably greater than the kinetic energy of their thermal motion. As a result, an ordered crystalline structure appears, which corresponds to the minimum of the free energy.

Ionic and covalent bonds are responsible not only for keeping atoms in a molecule, but also for retaining molecules and atoms in a solid. As a result, the crystalline structure of the solid is formed. If this structure is determined by the covalent bond, the crystals are called covalent, while if it is determined by the ionic bond, we have ionic crystals. The mechanism of formation of the covalent bond indicates that the electrons in covalent crystals are not strictly localized near the ions constituting the crystal lattice. The electrons responsible for the covalent bond are distributed among ions, being concentrated along certain directions called the directions of the bonds. This concept will be useful in Sec. 49 for describing macromolecules. The electron cloud in ionic crystals is localized in the vicinity of ions, while in the interstitial space the electrons are practically absent. An ionic crystal can be modelled by a set of impenetrable charged

!

There is no universal law for describing the intermolecular interaction. It depends on the properties of molecules, the conditions of interaction, its mechanism, and other factors. For this reason, the intermolecular interaction is always described by approximate formulas with strictly defined limits of their applicability.

The ionic bond is formed as a result of a complete exchange of charges, while the covalent bond is characterized by a partial exchange. Van der Waals forces are not associated with a charge exchange. The metallic bond is covalent in its physical nature, but in this case many electrons are collectivized.

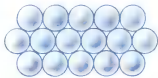


Fig. 60. Dense packing of ions of the same radius

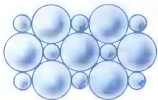


Fig. 61. Arrangement of ions with the ratio of radii equal to $\sqrt{2} + 1$

spheres subjected to the action of the Coulomb forces, the decisive role being played by the forces of attraction between oppositely charged spheres. The impenetrability of the spheres rules out their collapse.

The impenetrability of the spheres can be explained theoretically by the Pauli exclusion principle and the existence of stable electron configurations in atoms and molecules. The repulsive forces which balance the Coulomb forces of attraction emerge when the spheres come into contact. Moreover, the separations between the centres of the spheres must be minimal to ensure the minimization of the free energy for obtaining a stable equilibrium. This requirement determines the mode of "packing" the spheres which model the ions during the crystal structure formation. Figure 60 illustrates a possible mode of packing spheres of identical radius. If there are two types of ions with different radii, they can be packed in various ways. The most typical examples are shown in Figs. 61-63. We shall just say a few words about the packing shown in Fig. 62. Small balls are as if "suspended" without touching the neighbours. This means that the Coulomb forces acting on them seem to balance each other.

One should not think that this situation is in contradiction to the well-known Earnshaw theorem from the theory of electromagnetism. According to this theorem, a static equilibrium of electric charges is impossible. The given system involves, in addition to Coulomb's forces, "elastic" forces appearing as a result of contact of the spheres. Although these forces are also of electromagnetic origin, they cannot be completely reduced to it. Moreover the structure as a whole is dynamic and hence does not contradict the Earnshaw theorem.

The next type of crystals are molecular crystals which have molecules at the lattice sites. In this case very weak forces, called the Van der Waals forces, act between the molecules. The origin and peculiarities of these forces will be considered somewhat later in this section. For the present, it is sufficient to note that these forces are weak in order to emphasize that molecular crystals have relatively low strength.

In metals, or metallic crystals, the covalent bond is so strong that the density of electrons between ionic skeletons attains considerable values, and the electrons participating in the bonds between ions are practically not bound to the ions from which they originate. It can be assumed that these electrons are common to the entire crystal and form the electron gas. The bond appearing in this case is called the metallic bond.

These types of bonds do not exhaust the variety of bonds

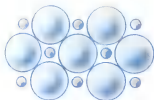


Fig. 62. Arrangement of ions with a large difference in radii



Fig. 63. Arrangement of ions with different radii in the case when the distance between the nearest neighbours is equal to the sum of their ion radii

existing in crystals. It is often impossible to assign a certain type of bonds to materials with a quite complicated crystal structure. Besides, even if one of the bonds dominates, other types may also play a certain role. For example, metals exhibit some features of covalent and molecular bonds. Moreover, in some cases it is insufficient to take into account only interactions between pairs. Unpaired interactions attenuate with distance much quicker than paired forces between the molecules, but they do play an important role in some cases.

Hydrogen bond plays a significant role in the bond formation in solids. Although it does not constitute a new type of bonds, it is expedient to put it in a separate category. This is due to the peculiarities of the atomic structure of hydrogen. Firstly, the hydrogen ion is a proton whose size is 10^5 times smaller than any other ion. Hence, this ion can practically be treated as a point mass. Secondly, the electron in a hydrogen atom is tightly bound to the ionic skeleton (proton). The ionization potential of atomic hydrogen is about 13.5 eV, which is several times higher than the ionization potential of other atoms. This means that in the formation of ionic crystals the hydrogen atom behaves not in the same way as other elements; in particular, the proton "settles" directly on the surface of a negative ion, giving rise to structures which are impossible with any other ions.

Under appropriate conditions, a proton may, for example, ensure the forces of attraction appearing between two negatively charged ions according to the schematic diagram shown in Fig. 59. Naturally, the electron must not "prevent" the appearance of this attraction. The essence of the hydrogen bond is that the electron and the proton move in such a way as to create bonds in a crystal, which are called hydrogen bonds. An important circumstance in the formation of hydrogen bonds is that the shell containing two electrons is the first filled shell in the Coulomb field. Hence, the hydrogen atom may form only one covalent bond, which is significant for characterizing the structure of corresponding crystals.

STRUCTURE OF LIQUIDS. In liquids, as well as in gases, the molecules are not linked by stationary stable bonds, and may change their relative positions. In gases, the distance between molecules is on the average large, and they rapidly change their mutual positions. In liquids, the distance between the molecules is small, they are densely packed in the volume occupied by the liquid, and change their mutual arrangement comparatively slowly. For relatively large intervals of time, groups of molecules may form aggregates which in their properties resemble a solid. Thus, in their

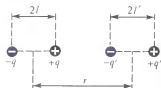


Fig. 64. Emergence of the Van der Waals forces

$$U(r) = \frac{a_1}{r^n} - \frac{a_2}{r^m}.$$

structure and intermolecular forces, liquids have the properties of a gas as well as of solids.

For this reason, the theory of liquids is the most difficult and the least developed.

VAN DER WAALS FORCES. The forces of attraction acting between molecules at comparatively large distances are called Van der Waals forces. These forces appear because a slight displacement of negative and positive charges in a neutral molecule violates its electric neutrality and the molecule becomes a dipole, viz. the system of equal and opposite charges separated by a very short distance (Fig. 64). A dipole is characterized by an electric moment equal to the product of the charges and the distance between them. In the surrounding space, the dipole creates an electric field determined by the fields of the two dipole charges. Clearly, the intensity of this field differs from zero, since the distance from points in space to the charges of the dipole are different, and hence the fields of the unlike charges of the dipole do not compensate one another. On the other hand, if a dipole is in an external field, this field acts on the dipole only if it is nonuniform.

There are molecules which possess a permanent dipole moment. Such molecules are called polar. When they are approaching each other, they tend to turn in such a way that the ends facing each other are oppositely charged. It can be easily seen that if the ends facing each other have like charges, such a mutual orientation is unstable. On the other hand, it can be easily verified that the total force of attraction between the dipole charges will be greater than the total force of repulsion when polar molecules have unlike charges on the opposite faces. Consequently, polar molecules attract each other, and such forces are called dipole orientation forces.

If molecules do not have a permanent dipole moment, they acquire it in an external electric field. In this field, the positive charges of a molecule are slightly displaced in the direction of the field, while the negative charges are shifted in the opposite direction. As a result, if the external field is nonuniform, a neutral molecule experiences the action of the electric field. The appearance of a dipole moment in a molecule under the effect of the field is called polarization. When nonpolar molecules approach each other, the electric fields of their charges rapidly vary with time and they compensate each other at various points of space only on the average. Hence, the approaching molecules polarize one another and the ends of polarized molecules facing one another have opposite charges. Mutually polarized molecules attract each other. Such forces are called dispersive (this term

! If the mean kinetic energy of molecules is lower than the absolute value of the mean energy of their mutual attraction, i.e. if the mean total energy of molecules (interaction energy + kinetic energy) in a system is negative, they form a bound state viz. either a liquid or a solid.

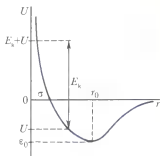


Fig. 65. Intermolecular potential

owes its origin to the dispersion of light, i.e. the change in the velocity of light and the refractive index of the medium depending on the frequency, which is also caused by the polarization of molecules).

INTERMOLECULAR POTENTIAL. Repulsive forces act at small distances between molecules. This is just a reflection of the fact that a molecule occupies a certain volume in space and prevents other molecules from penetrating into this region. The repulsive forces become noticeable in a very small region of the order of dimensions of a molecule. Figure 65 shows the variation of the potential energy of interaction depending on the distance r between molecules. For $r > r_0$, the forces of attraction act between the molecules, while for $r < r_0$ the repulsive forces come into play. A more precise form of the $U(r)$ dependence can be obtained only for specific molecules. There are no universal formulas for $U(r)$ suitable for all molecules. Usually, the function $U(r)$ is approximated by the following formula:

$$U(r) = a_1/r^n - a_2/r^m, \quad (29.3)$$

where the constants a_1 , a_2 , n , and m are chosen in accordance with the requirements of better approximation of the real potential. An analysis of potentials revealed that in most cases, $n = 12$ and $m = 6$ is the best approximation, a_1 and a_2 being specified for particular atoms. In this case the potential is written in the form

$$U(r) = 4\epsilon_0 [(\sigma/r)^{12} - (\sigma/r)^6] \quad (29.4)$$

and is called the Lennard-Jones potential. It is widely used in the theory of liquids and gases. The meaning of the quantities σ and ϵ_0 is illustrated in Fig. 65. In the form (29.4), we have a two-particle potential. It is used when we assume that the force of interaction between two molecules does not change in the presence, for example, of a third molecule. Strictly speaking, however, it is clear that it cannot be true, since the third molecule causes a rearrangement of positive and negative charges in molecules (polarization), and hence changes the interaction between the molecules. But if we take into account many-particle forces, this will considerably complicate the theoretical investigation of the problem. Therefore, although it is well known beforehand that many-particle forces often play a very important role in liquids, the study of intermolecular interaction is limited to

the consideration of effective two-particle forces which take into account the effect of many-particle forces to a certain extent.

The dependence of the Van der Waals forces on the distance can be estimated in the following way. Figure 64 shows that the forces of interaction are directed along the line connecting the molecules. The field intensity E at a distance r from the centre of the molecule is

$$\begin{aligned} E(r) &= \frac{1}{4\pi\epsilon_0} \left[\frac{q}{(r-l)^2} - \frac{q}{(r+l)^2} \right] \\ &= \frac{q}{4\pi\epsilon_0 r^2} \left[\frac{1}{(1-l/r)^2} - \frac{1}{(1+l/r)^2} \right], \end{aligned} \quad (29.5)$$

where q is the magnitude of charges separated in the molecule by the distance $2l$. Taking into account that

$$\frac{1}{(1 \pm l/r)^2} \approx 1 \mp \frac{2l}{r} \pm \dots, \quad (29.6)$$

we can limit ourselves to the first-order terms in l/r , since $l \ll r$. Then formula (29.5) assumes the form

$$E(r) = ql/(\pi\epsilon_0 r^3). \quad (29.7)$$

Let us now calculate the force with which this field acts on a polarized molecule (Fig. 64). Obviously,

$$\begin{aligned} F(r) &= [q'E(r+l) - q'E(r-l)] = \frac{qq'l}{\pi\epsilon_0} \left[\frac{1}{(r+l)^3} - \frac{1}{(r-l)^3} \right] \\ &= \frac{qq'l}{\pi\epsilon_0 r^3} \left[\left(1 + \frac{l}{r}\right)^{-3} - \left(1 - \frac{l}{r}\right)^{-3} \right]. \end{aligned} \quad (29.8)$$

Considering that $l \ll r$, we can put $(1 \pm l/r)^{-3} \approx 1 \mp 3l/r$. Formula (29.8) then assumes the form

$$F(r) = -6qlq'l/(\pi\epsilon_0 r^4). \quad (29.9)$$

The polarization of a molecule depends on the field. Assuming that it is proportional to the field intensity, we conclude that we must put $l \sim E \sim 1/r^3$ in (29.9). Hence, the force $F(r)$ is given by

$$F(r) \sim 1/r^7, \quad (29.10)$$

i.e. the Van der Waals forces rapidly decrease with increasing distance. According to (29.10), the potential of the Van der

Waals forces is inversely proportional to the sixth power of the distance between the molecules:

$$U(r) \sim 1/r^6. \quad (29.11)$$

Van der Waals forces appear when there is no charge exchange. Hence, when compared with the forces of ionic bond, they form another limiting case. The covalent bond appears as a result of a partial charge exchange and is intermediate between the ionic bond and the Van der Waals forces.

LIQUID AND GASEOUS STATES. MOLECULAR SYSTEMS. The potential energy of attraction between molecules is negative. If the sum of kinetic and potential energies of a molecular system under consideration is positive, the molecules left on their own tend to fly apart to an infinite distance. This corresponds to a tendency of a gas to expand.

When a gas is compressed, its density increases, and the average distance between the molecules decreases. It can be seen from (29.4) that the potential energy in this case will decrease. If the mean kinetic energy of the molecules is not very high, the sum of the kinetic and potential energies becomes negative at a certain moment of time. Such a molecular system cannot spontaneously dissipate in a large volume, since its energy would be only kinetic after dissipation, i.e. it would be positive, which is impossible in view of the fact that the total energy of the system is negative. In other words, we have a bound state in this case. Molecules cannot fly apart to large distances; on the contrary, they are confined near each other in a finite volume. The molecular system in such a state is either a liquid or a solid. In most cases (though not always), the liquid state is formed upon the compression of a gas.

This process of liquefaction of a gas upon compression may take place only if the kinetic energy of molecules is not very high, i.e. if the temperature is moderate. As a matter of fact, the minimum negative energy of interaction has a finite value (Fig.65). Consequently, at a sufficiently high temperature, the sum of the kinetic and potential energies of molecules can never be negative. This means that a gas cannot be liquefied just by an increase in the density when the temperature is sufficiently high. The temperature above which a gas cannot be liquefied by increase of pressure is called the critical temperature.

As pressure decreases, the process occurs in the reverse direction, i.e. the molecular system goes over from the liquid to the gaseous state.

?

1. Which physical factors cause a decrease in the Van der Waals forces in inverse proportion to the seventh power of the distance? Distribute these seven inverse powers among different factors.
2. What are many-particle forces and when is their role significant? Under which conditions is this role unimportant?
3. Why do molecular crystals include those with a very low binding energy?
4. Which properties make the liquids intermediate between solids and gases?

Sec. 30. LIQUEFACTION OF GASES

Experimental isotherms and two-phase region are considered. The properties of saturated vapour are described, as well as the dynamic nature of equilibrium between a vapour and its liquid. The properties of a substance in the critical state are analysed. The latent heat of transition is defined and the general characteristic of the first-order phase transitions is given.

EXPERIMENTAL ISOTHERMS. The theoretical conclusions drawn in Sec. 29 on the basis of an analysis of intermolecular interaction are confirmed by experimental studies. Figure 66 shows typical isotherms for a real gas, observed in experiments on gas compression.

Let us use this diagram to analyse the compression of the gas, say, at T_1 . As the gas is compressed to the volume V_1 , its pressure increases to p_1 . Upon a further decrease of the gas volume, a part of the gas liquefies, but the pressure remains equal to p_1 . Consequently, on the segment BC of the isotherm, the vessel contains liquid as well as the gas, separated by the interface which is the surface of the liquid. Physically homogeneous parts into which the system is separated are called phases. Hence, in the region CB the system consists of liquid and gaseous phases. At the point B , the entire volume is occupied by the gaseous phase, but as we move from B to C , the part of the volume occupied by the gaseous phase decreases, and the part filled by the liquid phase increases. At the point C the entire volume V_1 is filled by the liquid phase, i.e. the liquefaction of the gas is completed. A still further decrease in the volume is accomplished by compression of the liquid. Liquids offer a very strong resistance to compression, and hence a small decrease in the volume causes a considerable increase in pressure.

CRITICAL STATE. As the temperature increases, the segment of the two-phase isotherm becomes shorter. Finally, at a critical temperature T_{cr} , this segment contracts to a point. At this point, the difference between the liquid and the gas disappears, or, in other words, the liquid and the gas have the same physical properties. Such a state is called critical, and the quantities T_{cr} , p_{cr} , and V_{cr} are called the critical temperature, pressure and volume respectively. Above the critical point, the gas cannot be liquefied under any pressure. Above the critical pressure p_{cr} , the isotherm T_{cr} separates the gaseous and liquid states so that at the points of this isotherm the properties of the phases are identical. Hence, every time we cross the isotherm, a continuous transition from the gaseous to the liquid phase will occur.

TWO-PHASE REGION. In Fig. 66, the two-phase region is shown by the dashed curve passing through the points C , K , B , and A . This means that a transition from the gaseous to the liquid state can be performed either through the two-phase region or without it. For example, a transition from the gaseous state N to the liquid state M can be

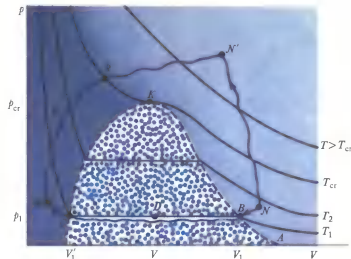


Fig. 66. Isotherms for a real gas and
■ liquid

performed either along $NBCM$, or along $NN'RM'M$. In the latter case, a transition to the liquid phase will take place at the point R , leaving behind the two-phase system. At this point, the properties of the liquid and the gaseous states are identical. However, these properties are different at the neighbouring points on both sides of the isotherm: on one side of the isotherm the substance is in the gaseous state and tends to expand, while on the other side it is a liquid and tends to retain its volume.

SATURATED VAPOUR. In a two-phase system, the liquid and its vapour are in dynamic equilibrium, and have quite definite densities and pressures at a particular temperature. The pressure p_1 is called the saturated vapour pressure (SVP) at the temperature T_1 . Figure 67 shows that the saturated vapour pressure increases with temperature. The vapour is called saturated, since it can hold no more substance at this temperature. If we try to make it "denser", a part of the saturated vapour liquefies. This is just the process that occurs in a two-phase system during a change in its volume.

SATURATED VAPOUR DENSITY. At the temperature T_1 (Fig. 66) the entire volume V_1 is filled by the saturated vapour, since even the slightest decrease in this volume converts a part of the vapour into liquid. Consequently, the saturated vapour density at this temperature is $\rho_{1g} = M/V_1$. At the temperature T_2 , the saturated vapour density is $\rho_{2g} = M/V_2 > \rho_{1g}$.

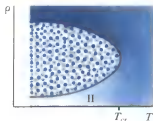


Fig. 67. Temperature dependence of the density of ■ liquid and of ■ saturated vapour:
I – liquid; II – saturated vapour

Thus, the saturated vapour density increases with temperature. If we consider a mole of gas molecules, the volumes V_1 and V_2 are the molar volumes, and M is the molar mass. If some other amount of gas molecules is taken, the volumes V_1 and V_2 are the volumes of the gas, and M is its mass. Similar remarks can be made about the volumes of liquids.

At the point C, the entire volume is occupied by the liquid. Consequently, the density of the liquid at T_1 is $\rho_{11} = M/V'_1$. It can be easily seen that the density of the liquid at the temperature T_1 is higher than the saturated vapour density at the same temperature. At the temperature T_2 , the density of the liquid is $\rho_{21} = M/V'_2 < \rho_{11}$. This means that with increasing temperature, the density of the liquid decreases.

As we approach the critical temperature, the difference in densities of the liquid and the gaseous phases decreases, and at the critical point the density of the liquid phase is equal to the density of the gaseous phase: $\rho_{cr} = M/V_{cr}$. The temperature dependence of the density of a liquid and its saturated vapour is shown in Fig. 67.

LEVER RULE. Let us consider the state of a two-phase system characterized by the point D (see Fig. 66). We denote the volume occupied by the system by V . Which part of this volume is filled by the liquid, and which part is filled by the gaseous state? Let us denote by V_l , V_g the volumes and by ρ_l and ρ_g the densities of the liquid and the gaseous phase respectively. The law of conservation of mass of a substance is written in the form

$$V_l \rho_l + V_g \rho_g = M. \quad (30.1)$$

Considering that $V_l + V_g = V$, we get

$$V_l (\rho_l - \rho_g) = M - V \rho_g. \quad (30.2)$$

Hence,

$$V_l = \frac{1 - V/V_1}{1/V'_1 - 1/V} = V'_1 \frac{V_1 - V}{V'_1 - V_1},$$

where $\rho_g = M/V_1$ and $\rho_l = M/V'_1$. Multiplying the right- and left-hand sides of the last equation by ρ_l and taking into account the fact that $\rho_l V_l = m_l$ and $\rho_l V'_1 = M$, where m_l is the mass of the liquid phase, we obtain

$$m_l = M (V_1 - V) / (V'_1 - V_1). \quad (30.3)$$

! In the critical state, the difference between the liquid and the gaseous states vanishes. This means that the substance does not offer resistance to a change in the volume and does not tend to increase it. It becomes as if indifferent to its density. This results in conditions favouring large density fluctuations.

The equilibrium between a liquid and its saturated vapour is dynamic and is maintained by a continuous exchange of substance between the phases.

Similarly,

$$m_g = M(V - V_1)/(V_1' - V_1). \quad (30.4)$$

This yields the ratio of the masses of the liquid and the gaseous phases:

$$m_l/m_g = (V_1 - V)/(V - V_1). \quad (30.5)$$

This ratio is inversely proportional to the distances from the point D to C and B : The removal of D from B corresponds to an increase in the mass of the liquid. Formula (30.5) is called the **lever rule**.

The real gas isotherms are similar to those shown in Fig. 66, but it is not always possible to plot them in such a form unless we use a special scale. For example, the densities of water and its saturated vapour at 50°C are respectively equal to 988.0 and $8.3 \times 10^{-2} \text{ kg/m}^3$, and the saturated vapour pressure is $122 \times 10^3 \text{ Pa}$. This means that the ratio of abscissas V_1/V_1' must be equal to 10^4 . Taking into account that the critical pressure of water $p_{cr} = 220.53 \times 10^5 \text{ Pa}$, we see that the ratio p_{cr}/p_1 of ordinates in the figure must be about 2000. Clearly, such a curve cannot be plotted in a diagram on linear scale. Hence, two-phase diagrams just reflect the nature of dependencies and behaviour of quantities rather than the real relation between the characteristics shown in the diagram.

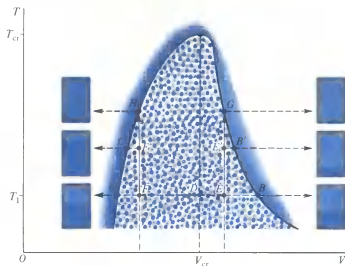
PROPERTIES OF A SUBSTANCE IN THE CRITICAL STATE. At the point K (critical state), the isotherm has a horizontal plateau (see Fig. 66). Consequently, $(\partial p/\partial V)_T = 0$, i.e. the pressure (density) does not depend on the volume. This means that if the number density of particles has increased in a certain region, the forces of pressure that would tend to decrease this density do not appear, and conversely, a decrease in the density (pressure) does not lead to the emergence of factors which would tend to restore the initial equilibrium state. As a result, the density fluctuations in the critical state become very large. This gives rise to critical opalescence.

CRITICAL OPALESCENCE. If a gas is compressed in a transparent vessel and a light beam is passed through it, the transmitted light will form an image of the vessel on a screen. Since the coefficients of absorption for the liquid and the saturated vapour are somewhat different, the liquid and the gaseous phases and the interface between them will be clearly seen on the screen. Under certain conditions which will be specified below, the interface between the two phases of the system remains unchanged upon heating, i.e. the

?

1. What is the meaning of the statement that there are liquid and gas on both sides of the critical isotherm above the critical pressure?
2. Why can density fluctuations attain very high values in the critical state?
3. What is the nature of the dynamic equilibrium in a two-phase system?
4. Which factors determine the latent heat of transition on the molecular level?

Fig. 68. The behaviour of a two-phase system upon increasing temperature at constant pressure



fractions of the volume occupied by the liquid and the gaseous phase remain the same. As the system approaches the critical temperature, the interface becomes less and less sharp. Since at the critical temperature the difference between the liquid and the gaseous phase vanishes, it can be expected that the interface will disappear. However, instead of this, at the moment when the interface should disappear the entire volume of the vessel becomes opaque, and the screen shows a dark spot. This phenomenon is called critical opalescence. If we increase the temperature of the system further, in a certain short period of time the transparency is recovered, but the vessel contains the substance in gaseous phase only, and there is no interface.

Critical opalescence is explained by strong density fluctuations in the critical state. Because of this, the refractive index and the absorption coefficient of the medium change very sharply from point to point. As a result, light is strongly scattered and absorbed in the medium, which is the essence of the critical opalescence.

THE BEHAVIOUR OF A TWO-PHASE SYSTEM UNDER CHANGE IN TEMPERATURE AT A CONSTANT VOLUME. The mass of the substance in a volume V containing a two-phase system may in general be different. The mode of the process induced by the variation of temperature depends on the relation between the mass of a substance contained in the vessel and its volume (Fig. 68). If a substance having the critical density can fill the entire volume, i. e. if $m = \rho_{cr} V_{cr}$, the

state T_1 on the two-phase diagram of the system will correspond to the point D . As the temperature rises, this point moves along the vertical to the point T_{cr} . In this process, the vessel contains two phases, the interface between them being practically fixed. When the system attains the point T_{cr} , the substance goes over to the critical state, and critical opalescence is observed.

If the mass of a substance is less than what is necessary to fill the volume at a critical density ($m < \rho_{cr} V_{cr}$), the initial state of the substance is characterized by the point E . According to the lever rule, the part of the volume occupied by the liquid phase is proportional to the segment EB , while the part of the volume filled by the gaseous phase is proportional to the segment EC . As the temperature rises, and the system goes over through the point E' , the part of the volume occupied by the liquid decreases, while the other part filled by the gas increases. The interface between the liquid and the gaseous phase in the vessel goes down. When the system attains the temperature corresponding to the point G , the entire volume is filled by the gas, and a further increase in the temperature at the constant volume just heats the gas.

If the mass of a substance is greater than what is necessary for filling the vessel at a critical density ($m > \rho_{cr} V_{cr}$), the initial state of the gas is characterized by the point F . As the temperature rises, the part of the volume occupied by the gas decreases as a direct consequence of the lever rule. The interface between the liquid and the gas will go up in this case. When the point H is reached, the entire volume becomes filled by the liquid. A further increase in temperature at constant volume results in heating the liquid.

HEAT OF PHASE TRANSITION. In a two-phase system, the phases are in equilibrium at the same temperature. If the volume increases, a certain part of the liquid evaporates, but in order to keep the temperature constant, the system must receive an appropriate amount of heat from outside. Thus, in order to go over from the liquid phase to the gaseous phase, a system must receive heat without changing the temperature. This heat is spent to change the phase state of the substance and is called the heat of phase transition, or the latent heat.

The latent heat of transition is spent for overcoming the attractive forces or, in other words, for compensating the negative potential energy of attraction between molecules. Obviously, as the temperature increases, the latent heat of a fixed mass of a substance decreases and vanishes at the critical temperature.

FIRST-ORDER PHASE TRANSITIONS. Phase transitions accompanied by absorption or liberation of latent heat are called the first-order phase transitions. Besides, there exist other types of phase transitions which are not connected with the latent heat.

Sec. 31. CLAUSIUS-CLAPEYRON EQUATION

The derivation of the Clausius-Clapeyron equation is given and the limits of its applicability are discussed. An approximate integral of this equation is calculated and simplest applications are considered.

DERIVATION OF THE EQUATION. The saturated vapour pressure increases with temperature (see Sec. 30). However, a quantitative relation between these two quantities established by the Clausius-Clapeyron equation has not been derived by us so far.

Let us consider an infinitely small reversible Carnot cycle whose isotherms are the states of a two-phase system at temperatures T and $T - dT$ (Fig. 69). The work done in this cycle is

$$A = (V_1 - V_2) dp. \quad (31.1)$$

Consequently, the efficiency of this cycle will be

$$\eta = A/Q^{(+)} = (V_1 - V_2) dp/L, \quad (31.2)$$

where L is the latent heat of transition for a given mass of the substance. On the other hand, the efficiency of the Carnot cycle is given by

$$\eta = 1 - T_2/T_1 = 1 - (T - dT)/T = dT/T. \quad (31.3)$$

Equating (31.2) and (31.3), we obtain the equation

$$dp/dT = L/[T(V_1 - V_2)], \quad (31.4)$$

which is called the Clausius-Clapeyron equation. This equation relates the pressure at which a two-phase system is in equilibrium, with temperature. If the latent heat of transition L and the volumes V_2 and V_1 of liquid and gaseous phases respectively are known as functions of temperature, the solution of the differential equation (31.4) can be used to find the pressure as a function of temperature.

Equation (31.4) was first obtained in 1834 by the French engineer Clapeyron (1799–1864) who considered a cycle in which the working body is a "liquid + saturated vapour" system. This equation was later derived by Clausius (1822–1888) from the second law of thermodynamics.

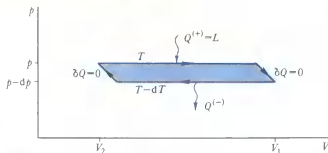


Fig. 69. To the derivation of the Clausius-Clapeyron equation

PHASE DIAGRAM. For a given mass, the volume V_1 of the vapour is larger than the volume of the liquid. Hence, $dp/dT > 0$ in (31.4). This means that the phase equilibrium pressure increases with temperature. Figure 70 shows the curve $p(T)$ whose points define a certain relation between the pressure and temperature, corresponding to the equilibrium state of a two-phase system. This curve is called the **phase diagram**.

The curve originates at the point A . This is the triple point, at which three phases (liquid, gas, and solid) are in equilibrium. It should be noted that in addition to the curve under consideration, two more curves (not shown in the diagram) converge at this point. The curve $p = p(T)$ terminates at the point K which corresponds to the critical state (see Sec. 30). There are two ways in which the system may go over from the gaseous state (point N) to the liquid state (point M). If the transition occurs along NRM , the system must pass through a two-phase state. However, the two-phase states can be by-passed in a transition from the point N to the point M , if we follow the path $NN'R'M'M$. The point R' corresponds to a transition from the gaseous to the liquid state. However, this transition occurs at the critical temperature, when there is no difference between the liquid and the gaseous states, and there is only one phase in the transition process. These two types of transition from N to M were already considered in the p - V diagram (see Fig. 66).

FIELD OF APPLICATION. The Clausius-Clapeyron equation (31.4) can, according to its derivation, be applied not only to the liquid-vapour phase transition, but to all first-order phase transitions. Another example of a first-order phase transition is crystallization, i.e. the transition of a substance from the liquid state to the solid state. This process involves the latent heat of crystallization (fusion). Hence Eq. (31.4) is also applicable to this system. We adopt this procedure while considering liquid-solid transitions (see Chap. 5).

$$\frac{dp}{dT} = \frac{L}{T(V_1 - V_2)}$$

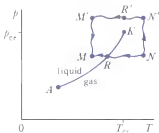


Fig. 70. Phase diagram of the liquid-vapour transition

APPROXIMATE SOLUTION OF THE CLAUSIUS-CLAPEYRON EQUATION. In order to solve Eq. (31.4), we must first of all find the temperature dependence of the heat of evaporation. There are two ways of transition from the liquid state at temperature T_0 and pressure p_0 to the vapour state at temperature T and pressure p : by evaporating the liquid at temperature T_0 and by heating the vapour under constant pressure to the temperature T . The energy expended per mole is equal to

$$\Delta Q_1 = L_0 + C_p(T - T_0),$$

where L_0 is the heat of evaporation which at T_0 is approximately equal to the evaporation heat of the saturated vapour at pressure p_0 . In the first case, the liquid is first heated to T and then evaporated. The heat of evaporation at T is denoted by $L(T)$. In the second case, the amount of energy expended is equal to

$$\Delta Q_2 = C_1(T - T_0) + L(T).$$

It follows from the law of conservation of energy that $\Delta Q_1 = \Delta Q_2$, i.e.

$$L_0 + C_p(T - T_0) = C_1(T - T_0) + L(T), \quad (31.5)$$

whence

$$L(T) = L_0 + (C_p - C_1)(T - T_0). \quad (31.6)$$

Equation (31.4) then assumes the form

$$\frac{dp}{dT} = \frac{L_0 + (C_p - C_1)(T - T_0)}{T(V_{m1} - V_{m2})}. \quad (31.7)$$

The molar volume of the liquid can be neglected in comparison to the molar volume of the gas ($V_{m2} \ll V_{m1}$), while for the vapour we can use the ideal gas equation which is applicable to the unsaturated vapours: $V_{m1} = RT/p$. Taking this into account, we can rewrite (31.7) as follows:

$$\frac{dp}{dT} = \frac{p}{RT^2} [L_0 + (C_p - C_1)(T - T_0)],$$

whence

$$\int_{p_0}^p \frac{dp}{p} = \frac{1}{R} \int_{T_0}^T \frac{L_0 + (C_p - C_1)(T - T_0)}{T^2} dT. \quad (31.8)$$

Integrating, we get

$$\ln \frac{p}{p_0} = \frac{L_0 - (C_p - C_1) T_0}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) + \frac{C_p - C_1}{R} \ln \frac{T}{T_0}. \quad (31.9)$$

The accuracy of these formulas can be judged from the following data. The pressure of the saturated water vapour at 100°C is 1.013×10^5 Pa, while the heat of vaporization is equal to 2.25 MJ/kg. With the help of formula (31.6) we find that the heat of vaporization $L(T)$ at 150°C is equal to 2.12 MJ/kg, the experimentally obtained value being 2.11 MJ/kg. Formula (31.9) gives the value 4.55×10^5 Pa for the pressure, compared to the experimental value of 4.76×10^5 Pa. These discrepancies are mainly due to the ideal gas approximation. The error increases as we approach the critical state.

Example 31.1. The boiling point of water at a pressure 1.013×10^5 Pa is equal to 100°C , while at 1.05×10^5 Pa, it is equal to 101°C . Upon vaporization at a pressure 1.013×10^5 Pa, the specific volume increases from 1.04×10^{-3} to $1.673 \text{ m}^3/\text{kg}$. Find the heat of vaporization at this pressure.

We use the Clausius-Clapeyron equation (31.4) in the following form:

$$l = \frac{\Delta p}{\Delta T} T(v_1 - v_2).$$

At $\Delta p = 37 \text{ GPa}$, $\Delta T = 1 \text{ K}$, $T = 373 \text{ K}$, and $v_1 - v_2 = 1.672 \text{ m}^3/\text{kg}$, we get $l = 2.29 \text{ MJ/kg}$. The discrepancy with the experimental value 2.25 MJ/kg is due to the use of finite differences.

Sec. 32. VAN DER WAALS EQUATION

The nature of deviation of the properties of a gas from the ideal behaviour is described. The physical factors taken into account by the Van der Waals equation are discussed.

The main peculiarities of the liquid state are analyzed with the help of the Van der Waals equation.

The theoretical results are compared with the experimental data.

DEVIATION OF THE PROPERTIES OF A GAS FROM THE IDEAL BEHAVIOUR. Experimental investigations of gases over a wide range of pressures have shown that pV is not constant at $T = \text{const}$, as it should be according to the ideal gas equation. The product pV changes with pressure as if the gas is compressed more readily than the ideal gas under low pressures, while it offers greater resistance to compression at high pressures in comparison to the ideal gas. In other words, auxiliary forces of attraction appear in a gas at low densities, while at high densities, repulsive forces come into play. These results of experimental investigations confirm the general nature of the potential energy curve describing the intermolecular interaction (see Fig. 65).

COMPRESSIBILITY. The compressibility κ is defined as the proportionality factor between the relative variation of volume $\Delta V/V$ and the change in pressure Δp :

$$\Delta V/V = -\kappa \Delta p, \quad (32.1)$$

whence

$$\kappa = -\frac{1}{AV} \left(\frac{\partial V}{\partial p} \right)_T. \quad (32.2)$$

For an ideal gas, $(\partial V/\partial p)_T = -V/p$, and hence $\kappa = 1/p$. It has been shown experimentally that the compressibility of a real gas under low pressure is higher than that for an ideal gas. Under high pressures, on the other hand, a real gas has lower compressibility than an ideal gas.

The compressibility of liquids is very small, since the molecules in liquids are densely packed. Consequently, very high pressures are required even for small variations of the volume of a liquid. For example, the compressibility of water is $0.47 \times 10^{-9} \text{ Pa}^{-1}$, the corresponding values for gasoline, glycerine, and acetone being 0.82×10^{-9} , 0.22×10^{-9} , and $1.27 \times 10^{-9} \text{ Pa}^{-1}$ respectively. Thus, the compressibility of liquids is about 1000 times smaller than that of gases.

VIRIAL EQUATION OF STATE. The equation of state depends on the law of interaction between molecules. Hence, strictly speaking, each type of molecules has its own equation of state. There is no universal equation of state for gases with intermolecular interaction and for liquids. In principle, the exact equation of state can be represented in the form of a virial equation of state

$$pV_m = RT + A_1(T)/V_m + A_2(T)/V_m^2 + \dots, \quad (32.3)$$

where $A_i(T)$ are the virial coefficients. This equation is an infinite series in inverse powers of the molar volume and requires the knowledge of an infinite number of virial coefficients. In this sense, this equation is important only from the theoretical point of view. For practical calculations, we must confine ourselves to the first few terms. Very many different approximate equations of state were used for investigating specific substances. Among the approximate equations of state, the Van der Waals equation received the widest recognition. It takes into account the main physical characteristics of the gas with interacting molecules in the simplest and the most compact form, and represents them in the most visual form.

VAN DER WAALS EQUATION. The ideal gas equation $pV = (m/M)RT$ does not take into account the long-range

forces of attraction between molecules or the short-range forces of repulsion. On account of the forces of repulsion, a molecule does not allow another molecule to penetrate the volume occupied by it. Consequently, the repulsive forces are characterized by the effective volume of a molecule. We denote by mb' the total effective volume of molecules which is proportional to the mass of the gas. In this case, the finite volume of molecules or, in other words, the repulsive forces, can be taken into account by considering that only the part $V - mb'$ of the volume V may change in the ideal gas equation.

The forces of attraction create an additional pressure on the gas. The molecules at the boundary of the gas in a vessel are attracted by other molecules inside the vessel, thus causing an effective additional pressure proportional to the number of particles per unit area of the boundary, and to the force with which the particles near the boundary are drawn inward by other particles. Obviously, this force is proportional to the number of particles taking part in its creation. In turn, the number of such particles is also proportional to the concentration n_0 of the particles. Hence, the additional pressure in the gas due to the forces of attraction is proportional to n_0^2 , i.e. inversely proportional to the square of the specific volume ($\propto m^2/V^2$).

Taking into account the above two corrections, we can transform the equation of state for an ideal gas into the Van der Waals equation (1873):

$$(p + m^2 a' / V^2)(V - mb') = (m/M) RT, \quad (32.4a)$$

where a' and b' are constants having different values for different gases. They are called the **Van der Waals constants**. Dividing both sides of Eq. (32.4a) by m , we get

$$\left(p + \frac{a'}{v^2}\right)(v - b') = R_0 T, \quad (32.4b)$$

where $v = V/m$ is the specific volume, and $R_0 = R/M$ is the specific gas constant, equal to the ratio of molar gas constant to the molar mass.

In place of constants a' and b' in Eq. (32.4a), the constants $a = a'/M^2$ and $b = b'/M$ are often used. In this case, considering that $v = m/M$, Eq. (32.4a) assumes the form

$$\left(p + \frac{v^2 a}{V^2}\right)(V - vb) = vRT, \quad (32.4c)$$

where a and b are also called the **Van der Waals constants** and should not be confused with the constants a' and b' .



The gas constant appearing in the Van der Waals equation has different values for different substances, and is not equal to the molar gas constant. Individual values of the gas constant are smaller than the molar values, thus indicating that molecules combine to form complexes near the critical state. Away from the critical state, the universal gas constant can replace the gas constant in the Van der Waals equation.

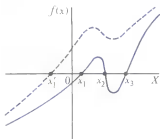


Fig. 71. To the determination of the roots of a third-degree polynomial

Considering that $V_m = V/v$, we can transform Eq. (32.4c) into

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT, \quad (32.4d)$$

which is a frequently encountered form of this equation.

If the specific volume and Eq. (32.4b) are used, the formulas contain the constants a' and b' . In the calculations involving the molar volume obtained from Eq. (32.4d), we must use the constants a and b . This fact should always be borne in mind.

Formulas (32.4b) and (32.4d) are of the same form. Hence, in order to simplify the notation and to make the formulas more general, the constants in them are denoted by a and b , and the gas constant R and volume V are used without subscripts. If V is taken for the molar volume, the formula has the sense of (32.4d), while if V indicates the specific volume, the formula has the sense of (32.4b), i.e. in this case R stands for R_0 and a and b for a' and b' .

VIRIAL FORM OF THE VAN DER WAALS EQUATION. The Van der Waals equation (32.4d) can be written as follows in the virial form (32.3):

$$pV_m = RT + \frac{RTb - a}{V_m} + RT \sum_{n=2}^{\infty} \frac{b^n}{V_m^n}. \quad (32.5)$$

This equation is obtained from (32.4d) if we use the series expansion

$$\frac{1}{1 - b/V_m} = \sum_{n=0}^{\infty} \left(\frac{b}{V_m}\right)^n, \quad (32.6)$$

which can always be carried out, since (b/V_m) is always less than unity in Eq. (32.4d). Thus, the Van der Waals equation is obtained analytically from the virial equation (32.3) by summing all its terms for a particular case when this summation is possible. It is more convenient to express Eq. (32.4d) in a different form for analyzing the isotherms. Multiplying both sides of this equation by V_m^2 and removing the brackets, we get

$$V_m^3 - (b + RT/p)V_m^2 + aV_m/p - ab/p = 0. \quad (32.7)$$

This is a third-order equation in V_m .

THE PROPERTIES OF THIRD-DEGREE POLYNOMIALS. Let us consider a polynomial

$$f(x) = x^3 + A_2x^2 + A_1x + A_0, \quad (32.8)$$

isotherms of a gas at a temperature above T_{cr} . For $T < T_{cr}$, the isotherms are considerably different from the isotherms observed experimentally for a real gas (see Fig. 66). Let us consider these in greater detail by taking the isotherm T_1 as an example.

On the region CB , the pressure increases with volume ($\partial p/\partial V > 0$). Obviously, this system cannot be in a stable equilibrium at any point on this region, since the slightest density fluctuations will be spontaneously amplified. Hence, the region CB cannot be in a stable state. In the regions $D'DC$ and BAA' , the pressure decreases with increasing volume, $(\partial p/\partial V) < 0$, and hence the corresponding states can physically exist. In this case, $(\partial p/\partial V)_T < 0$ is the necessary condition for stable equilibrium, although it may not always be a sufficient condition. It can be asked as to how a system can go over from the first to the second region if the intermediate region is absolutely unstable.

It was shown experimentally (see Fig. 66) that the system undergoes this transition through a two-phase state, the isotherm in this transition being horizontal (Fig. 72, segment DA). The only problem is to find the level at which the straight line must be drawn.

A transition from D to A can be accomplished via the isotherm DFA or the isotherm $DCBA$ which does not exist in a stable state. However, the states through which it passes are characterized by a specific volume, pressure, entropy, etc. The entropy in the states A and D has definite values. If both the transitions are carried out reversibly, we can write for identical entropy variations

$$\int_{DFA} \frac{\delta Q}{T_1} = \int_{DCBA} \frac{\delta Q}{T_1}. \quad (32.9)$$

Considering that $T_1 = \text{const}$ and $\delta Q = dU + p dV$, we obtain from (32.9)

$$U(A) - U(D) + \int_{DFA} p dV = U(A) - U(D) + \int_{DCBA} p dV, \quad (32.10)$$

where dU is the exact differential. Consequently, the horizontal line DFA must be drawn in such a way that the following equation is satisfied:

$$\int_{DFA} p dV = \int_{DCBA} p dV. \quad (32.11)$$

This means that the areas bounded by the curve $DCBA$ and the straight line DFA must be identical or, in other words,

the work done upon transitions along these two paths must be the same. This will be true if the areas bounded by the closed curves $DCFD$ and $FABF$ are equal.

METASTABLE STATES. It is now clear that the segments $A'A$ and DD' of the Van der Waals isotherms describe the gaseous and the liquid state. It remains to be found which states correspond to the regions AB and CD of the isotherms, since $\partial p/\partial V < 0$ on these segments, and hence their existence cannot be ruled out. It is shown experimentally that such states can actually be realized. The regions AB and DC characterize the states of supercooled vapour and superheated liquid. A supercooled vapour is the state in which a substance must exist in the liquid state according to its parameters, but continues to remain in the gaseous state according to its properties, i.e. does not retain its volume but tends to expand like a gas. A superheated liquid is the state of a substance in which it must be a gas according to its parameters, but remains in the liquid state.

These states are not absolutely stable. Under a small external perturbation, the system rapidly goes over to the nearest stable state. Such states are called metastable.

These states can be experimentally realized as follows. If very pure vapour of a substance (for example, water) is prepared in a closed vessel and then cooled, a transition to the liquid state does not occur when the conditions for such a transition are attained (see Fig. 70, point R). A further decrease of temperature leads to the liquid state region (to the left of the curve AK), but the substance remains in the gaseous phase. If a small amount of ions of some other substance are introduced into the volume occupied by the gas, a rapid transition of a certain fraction of the gas to the liquid state takes place and can be observed in the form of a mist.

The superheated liquid state is obtained as follows. We take a very pure liquid which is free not only of impurities but also from microscopic air bubbles. The latter condition is attained through a prolonged boiling of the liquid as a result of which all microscopic bubbles are expelled. If the liquid prepared in this way is heated, a transition from the liquid to the gaseous state is not observed when the conditions for such a transition are attained. The parameters of the substance (temperature, pressure) correspond to the gaseous state, but the substance remains in the liquid state. If a small amount of foreign matter (for example, a pinch of chalk) is added to the liquid, a rapid transition of a certain part of the liquid to the gaseous state occurs over the entire volume, and is accompanied by a vigorous boiling of the liquid.

! Each gas with intermolecular interaction has its own equation of state. There is no universal equation of state for real gases.

The physical factors ensuring the existence of metastable states of supercooled vapour and superheated liquid will become clear after analyzing the dependence of the saturated vapour pressure on the liquid surface shape (see Sec. 34).

CRITICAL PARAMETERS. For $T > T_{cr}$, the Van der Waals equation (32.7) has only one real root, while for $T < T_{cr}$, this equation has three real roots in a certain domain of p . It is obvious (Fig. 72) that as the temperature increases the values of these three real roots become closer and ultimately merge into a single value at $T = T_{cr}$. Consequently, Eq. (32.7) assumes the following form for the critical state:

$$(V - V_{cr})^3 = 0 = V^3 - 3V_{cr}V^2 + 3V_{cr}^2V - V_{cr}^3. \quad (32.12)$$

A comparison of Eqs. (32.12) and (32.7) gives

$$3V_{cr} = b + RT_{cr}/p_{cr}, \quad 3V_{cr}^2 = a/p_{cr}, \quad V_{cr}^3 = ab/p_{cr}. \quad (32.13)$$

This is a system of three equations in three unknowns V_{cr} , p_{cr} , and T_{cr} . Its solution is

$$V_{cr} = 3b, \quad p_{cr} = a/(27b^2), \quad T_{cr} = 8a/(27Rb). \quad (32.14a)$$

Thus, the parameters of the critical state of a substance are expressed in terms of constants a and b of the Van der Waals equation.

Hence, there are three equations for two Van der Waals constants. These equations can be satisfied only if R is also determined by Eq. (32.14a). Solving these equations for a , b , and R , we obtain

$$a = 3p_{cr}V_{cr}^2, \quad b = V_{cr}/3, \quad R = 8p_{cr}V_{cr}/(3T_{cr}). \quad (32.14b)$$

If we use specific volumes, Eqs. (32.14a) retain their form, only the following substitution must be made: $a \rightarrow a'$, $b \rightarrow b'$, $V \rightarrow v$, and $R \rightarrow R_0$.

Equations (32.14b) show that the individual value for the gas constant R must be calculated for each real gas. Each of these individual values differs from the molar gas constant kN_A and is less than this value. Since the gas constant is proportional to the number of molecules per mole, it can be concluded that the number of structural units forming a gas constant decreases at the critical state, i.e. the molecules combine to form complexes. Away from the critical state, these complexes decompose and the individual gas constant becomes equal to the molar constant. Hence we can use the molar gas constant for R at large distances from the critical state. While analyzing phenomena in the vicinity of the critical state, the individual value of the gas constant must be used.

?

1. Enumerate the physical factors which make the compressibility of a real gas smaller than that of an ideal gas at a low pressure and larger at a high pressure.
2. On what basis can we choose the pressure at which a horizontal isotherm of a real gas corresponding to the two-phase state must be drawn?
3. Why are a supercooled vapour and a superheated liquid called the metastable states?

The values of critical parameters for some substances are listed in Table 2.

Table 2
Values of Critical Parameters

Substance	T_{cr} , K	p_{cr} , 10^5 Pa	V_{cr} , 10^{-3} m ³ /kg
Hydrogen	33.2	13.29	32.26
Nitrogen	126.0	33.93	3.22
Oxygen	154.3	50.34	2.32
Chlorine	417.1	77.08	1.75
Water vapour	647.25	220.53	2.50

LAW OF CORRESPONDING STATES. It is convenient to represent the Van der Waals equation (32.4) in a dimensionless form. Taking the critical volume, pressure, and temperature from (32.14a) as the respective units, we can write

$$V_r = V/V_{cr}, \quad p_r = p/p_{cr}, \quad T_r = T/T_{cr}, \quad (32.15)$$

where V_r , p_r , and T_r are dimensionless parameters for measuring the volume, pressure, and temperature respectively, of the substance under investigation. They are called the reduced parameters. Substituting (32.15) into (32.4), and taking into account (32.14b), we obtain

$$(p_r + 3/V_r^2)(3V_r - 1) = 8T_r. \quad (32.16)$$

Thus, if we take the critical parameters of a substance as units, the equation of state assumes the form (32.16) which is the same for all substances. It can be concluded from here that the behaviour of different substances is also the same. This circumstance played an important role in science at a certain time, because the knowledge of the behaviour of some substances could be used for predicting the behaviour of other substances. For example, this led not only to the prediction that hydrogen can be converted from the gaseous to the liquid state, but also to the estimate of temperature and pressure at which this becomes possible. The statement about the identical behaviour of all liquid-gas systems is called the law of corresponding states. Quantitatively, this law can be formulated as follows: if two reduced parameters of a substance are identical, the third parameter is also the same.

Consequently, the law of corresponding states is not only the verbal expression for the peculiarities of the dimensionless Van der Waals equation (32.16), but has a general significance independently of the Van der Waals equation, since the reduced parameters are determined independently of the equation of state of a substance. It must be remarked, however, that the law of corresponding states is not obeyed by real gases and liquids.

COMPARISON OF THE VAN DER WAALS EQUATION WITH THE EXPERIMENTAL RESULTS. The Van der Waals equation takes into account the main peculiarities of a substance in the liquid or gaseous state in a simple, visual, and convenient form. Hence, for several decades after its formulation in 1873, it played a leading role in the works on liquefaction of gases not only in the sense that it allowed an estimation of temperatures and pressures at which liquefaction is possible, but mainly because it led to the firm belief that liquefaction is in general possible.

Qualitatively, the Van der Waals equation describes the liquid-gas system very well, but quantitative predictions based on this equation deviate from the experimental results. The main differences are as follows:

1. For a given substance, the constants a and b in the Van der Waals equation must be independent of temperature. In actual practice, however, different values of a and b have to be chosen for isotherms corresponding to different temperatures, i.e. a and b depend on temperature.

2. It follows from Eq. (32.14a) that the quantity

$$p_{cr} V_{cr} (RT_{cr}) = 3/8 = 0.375 \quad (32.17)$$

must be a universal constant for all substances. However, it changes its value in actual practice. For example, it is equal to 0.23 for water and 0.31 for helium. In general, the agreement with the predictions of the Van der Waals equation is better for light gases than for heavy gases. This explains the success of the theoretical predictions concerning the liquefaction of hydrogen and helium, in which the experimental physicists were engaged at the beginning of the twentieth century.

3. The relation $V_{cr} = 3b$ is not obeyed. A more exact relation is $V_{cr} = 2b$.

4. In the region of two-phase equations, the Van der Waals equation is not proved theoretically and its results differ from the experiment.

As mentioned above, a universal equation of state cannot exist for all substances, and the Van der Waals equation never claimed to play the role of such an equation. However,

even for describing a specific substance, the Van der Waals equation is only an approximate equation of state.

THE INTERNAL ENERGY OF A VAN DER WAALS GAS. This energy consists of the internal energy of molecules constituting a gas and the kinetic energy of the motion of the centre of mass of molecules, which are together equal to $C_V T$, as well as the potential energy of mutual attraction of molecules, which has a negative value. It should be noted that the first part of the heat capacity can be expressed in the form $C_V T$ only if C_V is independent of temperature.

The potential energy of attraction is equal to the work done against the forces of attraction in order to separate the molecules to an infinitely large distance where it can be assumed that there is no interaction between them and that the potential energy of their interaction is equal to zero. The pressure due to the intermolecular attraction in the Van der Waals equation is equal to a/V^2 , and hence the potential energy of interaction is given by the formula

$$\int_{\infty}^V \frac{a}{V^2} dV = -\frac{a}{V}, \quad (32.18)$$

where the lower limit of integration is chosen in such a way that the potential energy corresponding to it is equal to zero. Hence the internal energy of a Van der Waals gas is given by

$$U = C_V T - a/V. \quad (32.19)$$

Of course, this formula can be derived from purely thermodynamic considerations also. We start with formula (23.28):

$$dU = C_V dT + [T(\partial p/\partial T)_V - p] dV. \quad (32.20)$$

It follows from the Van der Waals equation that

$$p = RT/(V - b) - a/V^2. \quad (32.21)$$

Hence

$$T \left(\frac{\partial p}{\partial T} \right)_V = \frac{RT}{V - b} = p + \frac{a}{V^2}. \quad (32.22)$$

Equation (32.20) then assumes the form

$$dU = C_V dT + \frac{a}{V^2} dV. \quad (32.23)$$

Considering that $U = 0$ for $T = 0$ and $V = \infty$, we obtain from Eq. (32.23)

$$U = \int_0^T C_V dT + \int_{+\infty}^V \frac{a}{V^2} dV = C_V T - \frac{a}{V}, \quad (32.24)$$

where C_V is independent of T .

INTERPRETATION OF QUANTITIES APPEARING IN THE VAN DER WAALS EQUATION. We introduce the equation of state of a gas whose statistical model is described in detail in Sec. 5. The maximum number of microscopic states corresponding to the equilibrium state of a system is given by formula (5.6):

$$\Gamma_0 = N!/(N-n)!, \quad (32.25)$$

the values of the quantities used in this formula and in subsequent formulas being the same as in Sec. 5. According to the Boltzmann relation (19.12), the entropy of such a system of molecules is

$$S = k \ln \Gamma_0 = k \ln [N!/(N-n)!] \\ \approx k [N \ln N - N - (N-n) \ln (N-n) + N - n], \quad (32.26)$$

where we have used Stirling's formula. Consequently,

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{l^3} \left(\frac{\partial S}{\partial N}\right)_T = \frac{k}{l^3} [\ln N - \ln (N-n)] \\ = -\frac{k}{l^3} \ln \left(1 - \frac{n}{N}\right) = -\frac{k}{l^3} \ln \left(1 - \frac{l^3 n}{N}\right) \\ = -\frac{k}{l^3} \ln \left(1 - \frac{b}{V}\right), \quad (32.27)$$

where $V = Nl^3$, l^3 is the volume of one of the unit cells into which the volume V is divided; $b = nl^3$ is the Van der Waals constant. With the help of one of the Maxwell relations (23.23), viz $(\partial S/\partial V)_T = (\partial p/\partial T)_V$, we can represent Eq. (32.27) in the form

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{k}{l^3} \ln \left(1 - \frac{b}{V}\right) = -\frac{nk}{nl^3} \ln \left(1 - \frac{b}{V}\right) \\ = -\frac{nk}{b} \ln \left(1 - \frac{b}{V}\right). \quad (32.28)$$

The law of corresponding states: if two reduced parameters of a substance are identical, the third parameter is also the same.

The pressure correction to the Van der Waals equation assumes that the intermolecular attraction extends to distances much larger than the molecular dimensions. However, experience shows that even at a distance equal to five times the diameter of a molecule, the forces of attraction are practically absent. Consequently, the Van der Waals equation can claim to give only a qualitative description of a real gas.

Integrating with respect to T for $V = \text{const}$, we obtain

$$p = -\frac{nkT}{b} \ln\left(1 - \frac{b}{V}\right) = nkT\left(\frac{1}{V} + \frac{b}{2V^2} + \frac{b^2}{3V^3} + \dots\right), \quad (32.29)$$

where $\ln(1 - b/V)$ is expanded into a series in $(b/V) < 1$. For $b = 0$, Eq. (32.29) coincides with the ideal gas equation, while for $b \neq 0$, it is reminiscent of the Van der Waals equation in which $a = 0$ and $1/(V - b)$ is replaced by $(1/b) \ln(1 - b/V)$.

In order to take into account the forces of attraction, we shall assume that the energy of interaction is the sum of the energies of interaction between pairs of molecules. The number of these pairs is proportional to n^2 . If all the cells of the volume under investigation were filled by molecules, i.e. $n = N$, the total energy of interaction should be proportional to the volume of the vessel, in accordance with the concept of additivity of energy. Hence, the energy of pairwise interaction between n molecules is proportional to n^2/N . In this case, the entropy remains unchanged, and the free energy will assume, in accordance with (23.18), the following form:

$$F = An^2/N - kT \ln [N!/(N - n)!], \quad (32.30)$$

where A is the proportionality factor. Substituting this expression into one of the formulas from (23.23), we get for pressure

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = -\frac{1}{V^3} \left(\frac{\partial F}{\partial N}\right)_T = -\frac{An^2}{V^3 N^2} + kT \frac{\partial}{\partial N} \frac{N!}{(N - n)!} = -\frac{a}{V^2} + \frac{nkT}{b} \ln\left(1 - \frac{b}{V}\right), \quad (32.31)$$

where $a = A/V^3 n^2$, and the differentiation is performed in the same way as in (32.27). Formula (32.31) is almost identical to the Van der Waals equation, the only difference being that $(1/b) \ln(1 - b/V)$ is substituted for $1/(V - b)$. The correction for pressure in the Van der Waals equation is made under the assumption that intermolecular attraction persists even at distances considerably exceeding the dimensions of a molecule. However, it is known from experiments that the forces of attraction between molecules practically vanish at distances of the order of five molecular diameters. This means that the Van der Waals equation is unable to provide a sufficiently accurate account of attractive forces between molecules, and can provide only a qualitative description.

Such an approximate method of describing the interaction between molecules, however, is widely used in other physical problems as well and is called the molecular field theory. It assumes that each molecule is in the potential field created by all the remaining molecules, and that the intensity of this field is proportional to the molecular density.

EQUATION OF STATE BASED ON THE VIRIAL THEOREM. The equation of state for simple liquids can be obtained in the general form with the help of the virial theorem. A liquid is called simple if its molecules are spherically symmetric and the intermolecular potential depends only on the distance between molecules (for example, the Lennard-Jones potential).

The equation of motion for each molecule has the form

$$\mathbf{F}_i = m d^2 \mathbf{r}_i / dt^2, \quad (32.32)$$

where $\mathbf{F}_i$ is the total force acting on the i th molecule, $\mathbf{r}_i$ is its radius vector, and m is the mass of a molecule. The reference point for radius vectors is arbitrary. Scalar multiplication of both sides of (32.32) by $\mathbf{r}_i$ gives

$$\mathbf{F}_i \cdot \mathbf{r}_i = m \mathbf{r}_i d^2 \mathbf{r}_i / dt^2. \quad (32.33)$$

Considering that

$$\mathbf{r}_i \frac{d^2 \mathbf{r}_i}{dt^2} = \frac{d}{dt} \left(\mathbf{r}_i \frac{d \mathbf{r}_i}{dt} \right) - \left(\frac{d \mathbf{r}_i}{dt} \right)^2 = \frac{1}{2} \frac{d^2}{dt^2} (r_i^2) - \left(\frac{d \mathbf{r}_i}{dt} \right)^2, \quad (32.34)$$

we can rewrite (32.33) in the form

$$\frac{m}{2} \frac{d^2}{dt^2} (r_i^2) = \mathbf{F}_i \cdot \mathbf{r}_i + m v_i^2, \quad (32.35)$$

where $v_i = d \mathbf{r}_i / dt$ is the velocity of the i th molecule. Adding these equations for all the molecules (the number of addends in the sum for one mole of molecules is N_A), we obtain

$$\sum_i \frac{m}{2} \frac{d^2}{dt^2} (r_i^2) = \sum \mathbf{F}_i \cdot \mathbf{r}_i + \sum m v_i^2. \quad (32.36)$$

Averaging both sides of this equation over time, we find that the left-hand side is equal to zero, since the molecules in a finite volume are in a steady state. Hence,

$$\left\langle \sum_i \mathbf{F}_i \cdot \mathbf{r}_i \right\rangle_t + \left\langle \sum_i m v_i^2 \right\rangle_t = 0. \quad (32.37)$$

The force acting on a molecule can be expressed as the sum of two forces:

$$F_i = F'_i + F''_i, \quad (32.38)$$

where F'_i is the force acting on the i th molecule from all the remaining molecules, and F''_i is the force acting on the molecule from the walls of the vessel, which confine the liquid to the vessel and give it the shape of the vessel (the force of gravity is absent).

In other words, the force F''_i takes into account the pressure exerted by the vessel walls on the liquid. Substituting (32.38) into (32.37), we get

$$\langle \sum_i F'_i r_i \rangle + \langle \sum_i F''_i r_i \rangle + \langle \sum_i m v_i^2 \rangle = 0. \quad (32.39)$$

We take the vessel in the form of a cube with an edge L . The origin is made to coincide with the centre of the cube, and the coordinate axes are parallel to the edges. Clearly, the force F'_i in this case will be nonzero only for $x_i = \pm L/2$, $y_i = \pm L/2$, and $z_i = \pm L/2$. Consequently, the second term in (32.39) assumes the form

$$\begin{aligned} \langle \sum_i F''_i r_i \rangle &= \langle \sum F''_{xi} x_i \rangle + \langle \sum F''_{yi} y_i \rangle + \langle \sum F''_{zi} z_i \rangle \\ &= (L/2) \langle \sum_{x=L/2} F''_{xi} \rangle - (L/2) \langle \sum_{x=-L/2} F''_{xi} \rangle + \dots, \end{aligned} \quad (32.40a)$$

where the dots stand for the terms corresponding to the other two coordinate axes.

Considering that the pressure is directed inwards in the liquid, we get

$$\langle \sum_{x=L/2} F''_{xi} \rangle = -pS = -pL^2, \quad \langle \sum_{x=-L/2} F''_{xi} \rangle = pS = pL^2, \quad (32.40b)$$

where $S = L^2$ is the area of a face of the cube. Since we are considering one mole of liquid molecules, the volume of the cube is equal to the molar volume of the liquid, i.e. $L^3 = V_m$. Relations similar to (32.40b) can be written for the Y - and Z -axes. Hence, (32.40a) assumes the form

$$\langle \sum F''_i r_i \rangle = -3pV_m, \quad (32.41)$$

while Eq. (32.39) can be written as follows:

$$\langle \sum F'_i r_i \rangle - 3pV_m = - \langle \sum m v_i^2 \rangle. \quad (32.42)$$

Further, we consider that the force F_i acting on the i th molecule is equal to the sum of forces acting on it from all the remaining molecules, i.e.

$$F_i = \sum_{j \neq i} F_{ji}, \quad (32.43)$$

where F_{ji} is the force acting on the i th molecule from the j th molecule. Taking (32.43) into consideration, we get

$$\begin{aligned} \sum_i F_i r_i &= \sum_{\substack{i, j \\ i \neq j}} F_{ji} r_i = \sum_{(\text{pairs})} (F_{ji} r_i + F_{ij} r_j) \\ &= \sum_{(\text{pairs})} F_{ji} (r_i - r_j) = \sum_{(\text{pairs})} F_{ji} r_{ji}, \end{aligned} \quad (32.44)$$

where $r_{ji} = r_i - r_j$ is the radius vector drawn from the j th molecule to the i th molecule. In (32.44), we have considered that $F_{ji} = -F_{ij}$ in accordance with Newton's third law of motion. Since the forces are central, the vectors F_{ji} and r_{ji} are collinear. Hence,

$$F_{ji} r_{ji} = F_{ji} r_{ji}, \quad (32.45)$$

where r_{ji} is the distance between the j th and the i th molecule, and F_{ji} is the magnitude of the force acting from the j th molecule on the i th molecule (it is positive for repulsive forces and negative for attractive forces).

According to the theorem of equipartition of energy, we can write

$$\langle \sum_i m v_i^2 \rangle = \sum_i 3kT = 3RT, \quad (32.46)$$

since the number of addends in the sum is equal to the Avogadro constant N_A . Taking into account (32.44)-(32.46), we can rewrite Eq. (32.42) in the form

$$pV_m = RT + \frac{1}{3} \langle \sum_{(\text{pairs})} F_{ji} r_{ji} \rangle. \quad (32.47)$$

If $\rho(r)$ characterizes the radial distribution of the concentration of molecules, the number of molecules in the layer of thickness dr at a distance r from the given molecule is equal to $4\pi r^2 \rho(r) dr$. Denoting the intermolecular potential by $U(r)$, we obtain

$$\langle \sum_{(\text{pairs})} F_{ji} r_{ji} \rangle = -r \frac{dU}{dr} 4\pi r^2 \rho(r) dr, \quad (32.48)$$

where $F_r = -dU/dr$ for central forces. In order to calculate the total contribution to the sum from the interaction of the i th molecule with all the remaining molecules, we must integrate (32.48) over all the molecules:

$$\langle \sum_j F'_{ji} r_{ji} \rangle = -4\pi \int_0^\infty \frac{dU(r)}{dr} r^3 \rho(r) dr, \quad (32.49)$$

where the forces of interaction sharply decrease with distance, and hence the limits of integration can be extended to infinity. Next, the summation over i must be carried out, which gives N_A quantities (32.49). Since each molecule was considered twice in the interaction, we get

$$\langle \sum_{(\text{pairs})} F'_{ji} r_{ji} \rangle = -\frac{N_A}{2} 4\pi \int_0^\infty \frac{dU(r)}{dr} r^3 \rho(r) dr. \quad (32.50)$$

Then the equation of state (32.47) assumes the form

$$pV_m = RT - \frac{N_A}{6} 4\pi \int_0^\infty \frac{dU(r)}{dr} r^3 \rho(r) dr. \quad (32.51)$$

The distribution of concentration $\rho(r)$ depends on the state of the liquid, i.e. on its pressure and temperature, for example. It can be seen from (32.51) that we must know $\rho = \rho(r, p, T)$ and the intermolecular potential $U(r)$ in order to find the equation of state. Formula (32.51) connects the macroscopic parameters of a liquid with its molecular characteristics (which may be independently measured in experiments) in the most general form. Hence, this formula provides a reliable basis for verifying the accuracy of the molecular-kinetic hypotheses about the structure of simple liquids.

COMPUTER EXPERIMENTS. With the advent of high-speed computers it became possible to theoretically investigate the properties of liquids without knowing their equations of state. If the intermolecular potential and forces acting on a molecule from other molecules are known, a sufficiently fast computer can easily calculate the motion of hundreds of molecules, taking their interaction into account. For this purpose, we choose quite small time intervals δt in which the molecular picture does not change appreciably. Usually, δt is of the order of 10^{-14} s.

At an average velocity of the order of 10^3 m/s, the distance traversed by a molecule during this time interval is equal to 10^{-11} m, which is about 10 times smaller than the diameter

of a molecule. The coordinates and the velocities of a particle change during this time by $\Delta r = \sqrt{\delta t} + F(\delta t)^2/(2m)$ and $\Delta v = F\delta t/m$. Adding these quantities to the previous values of coordinates and velocities, we obtain the new values, calculate the forces, and take the next step. And so on. Irrespective of the initial distribution of coordinates and velocities, we obtain Maxwell's velocity distribution after a few dozen or a few hundred steps. We can then use the data for coordinates and velocities of molecules to calculate all the characteristics, such as pressure, temperature, radial distribution $\rho(r)$ of the concentration of molecules, etc.

The results of such experiments are in good agreement with experimental data obtained for liquids by using the Lennard-Jones potential. The discrepancy between the theoretical and experimental results can be used to find even small deviations from the potential used for calculations and to introduce appropriate corrections. Thus, a computer can be used for an accurate modelling of the behaviour of a liquid and for investigating its properties under different conditions, i.e. for carrying out numerical experiments. Such methods are widely used at present for studying liquids.

The following physical processes occur in this case. Near the surface, there is a dynamic equilibrium, i.e. the number of molecules arriving at the surface per second from the inner regions is equal to the number of molecules leaving the surface per second for the inner regions. In order to go over from inner layers to the surface layer, a molecule must "push aside" the molecules of the surface layer and overcome the forces of attraction due to the inner layer molecules which strive to hold it back.

In order to go over from the surface layer to an inner layer, on the other hand, a molecule must simply "push aside" the inner layer molecules. Thus, it is more difficult for a molecule to go over from an inner layer to the surface than vice versa. Hence, the dynamic equilibrium is possible only if the density of molecules in the surface layer is less than the bulk density of the liquid.

Consequently, the surface layer is in a sort of stretched state. A decrease in the density of molecules in the surface layer is confirmed by experiments on the reflection of polarized light. The surface layer thickness is just a few molecular layers.

Example 32.1. Find the Van der Waals constants for hydrogen if it is known that its critical temperature $T_{cr} = 33.2$ K, the critical pressure $p_{cr} = 1.295$ MPa, and the molar volume in the critical state $V_{m,cr} = 6.5 \cdot 10^{-5}$ m³/mole.

On the basis of (32.14b), we can write:

$$a = 3p_{cr}V_{m,cr}^2, \quad b = V_{m,cr}/3, \quad R = 8p_{cr}V_{m,cr}/(3T_{cr}), \quad (32.52)$$

whence

$$\begin{aligned} a &= 3 \cdot 1.295 \cdot (0.065)^2 \cdot \text{Pa} \cdot \text{m}^6/\text{mole}^2 \\ &= 1.64 \cdot 10^{-2} \text{ Pa} \cdot \text{m}^6/\text{mole}^2, \end{aligned}$$

$$b = (6.5 \cdot 10^{-5})/3 \text{ m}^3/\text{mole} = 2.2 \cdot 10^{-5} \text{ m}^3/\text{mole},$$

$$R = \frac{8}{3} \frac{1.295 \cdot 10^6 \cdot 6.5 \cdot 10^{-5}}{33.2} \frac{\text{J}}{\text{mole} \cdot \text{K}} = 6.763 \text{ J}/(\text{mole} \cdot \text{K}). \quad (32.53)$$

It can be seen that the individual molar gas constant for hydrogen in the vicinity of the critical point differs considerably from the molar gas constant which is equal to 8.31 J/(mole·K).

Example 32.2. Find the hydrogen pressure from the Van der Waals equation for a molar volume $10^{-3} \text{ m}^3/\text{mole}$ at a temperature of 300 K, as well as for a molar volume $10^{-4} \text{ m}^3/\text{mole}$ at a temperature of 35 K.

In the first case, the state of the gas is far from critical, and hence we can use the molar gas constant:

$$\begin{aligned} p &= \frac{RT}{V_m - b} - \frac{a}{V_m^2} = \left[\frac{8.31 \cdot 300}{10^{-3} - 2.2 \cdot 10^{-5}} - \frac{1.64 \cdot 10^{-2}}{(10^{-3})^2} \right] \text{Pa} \\ &= 2.53 \cdot 10^6 \text{ Pa}. \end{aligned}$$

Under these conditions, the pressure of the ideal gas is

$$p = \frac{RT}{V_m} = \frac{8.31 \cdot 300}{(10^{-3})} \text{ Pa} = 24.93 \cdot 10^5 \text{ Pa}.$$

In the second case, the state of the gas is close to critical and the individual gas constant should be used ($R = 6.763 \text{ J}/(\text{mole} \cdot \text{K})$ for hydrogen, see (32.53)):

$$p = \left[\frac{6.763 \cdot 35}{10^{-4} - 2.2 \cdot 10^{-5}} - \frac{1.64 \cdot 10^{-2}}{(10^{-4})^2} \right] \text{ Pa} = 1.39 \cdot 10^6 \text{ Pa}. \quad (32.54)$$

The pressure of the ideal gas in this case is equal to

$$p = \frac{8.31 \cdot 35}{10^{-4}} \text{ Pa} = 2.91 \cdot 10^6 \text{ Pa}, \quad (32.55)$$

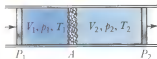


Fig. 73. Schematic diagram of the Joule-Thomson process

which is twice the pressure of the real gas. Hence, the individual gas constant is quite significant in the vicinity of the critical point.

Example 32.3. Given the Van der Waals constants and the individual gas constant for water vapour near the critical point: $a = 0.199 \text{ Pa} \cdot \text{m}^6/\text{mole}^2$; $b = 1.83 \times 10^{-5} \text{ m}^3/\text{mole}$; and $R = 5.008 \text{ J}/(\text{mole} \cdot \text{K})$. Find the parameters of the critical state.

Using formulas (32.14a), we get

$$p_{cr} = \frac{0.199}{27 (1.83 \cdot 10^{-5})^2} \text{ Pa} = 22 \text{ MPa},$$

$$V_{m cr} = 3 \cdot 1.83 \cdot 10^{-5} \text{ m}^3/\text{mole} = 5.5 \cdot 10^{-5} \text{ m}^3/\text{mole},$$

$$T_{cr} = \frac{8 \cdot 0.199}{27 \cdot 5.008 \cdot 1.83 \cdot 10^{-5}} \text{ K} = 643 \text{ K}.$$

In order to describe the behaviour of vapour at room temperature, we can use the molar gas constant, but in this case, we must take the following values for the Van der Waals constants:

$$a = 0.554 \text{ Pa} \cdot \text{m}^6/\text{mole}^2; \quad b = 3.1 \cdot 10^{-5} \text{ m}^3/\text{mole}. \quad (32.56)$$

Sec. 33. JOULE-THOMSON EFFECT

The physical significance and mathematical calculations of the differential and integral Joule-Thomson effect are discussed. The applications of the effect to liquefaction of gases, as well as the properties of a substance near 0 K, are considered.

THE PHYSICAL CONTENT OF THE EFFECT. During expansion, a gas performs work. If the gas is isolated, the source of work is the internal energy. If the entire internal energy were reduced to the kinetic energy of particles, the temperature of the gas should decrease. If the expansion of the gas occurred without accomplishing work, the gas temperature should remain unchanged. The expansion without heat exchange can be realized as follows.

Suppose that we have a cylinder (Fig. 73) divided into two parts by the porous plug A. The same gas occupies the volumes V_1 and V_2 at different pressures on both sides of the plug. If $p_1 > p_2$, the gas slowly percolates through the porous plug from volume V_1 to volume V_2 . In order to maintain the pressures p_1 and p_2 at a constant level, the piston P_1 must be pushed into the cylinder, thus reducing the volume V_1 and performing work over the gas, while the piston P_2 must be pulled out, thus forcing the gas to perform work. For an ideal gas, the work done on the gas due to the motion of the piston P_1 is equal to the work done by the gas due to the motion of the piston P_2 in accordance with Boyle's law: $p_1 |\Delta V_1| = p_2 |\Delta V_2|$ ($T = \text{const}$).

Things are different in a real gas, where the internal energy also contains the potential energy of intermolecular interaction. Figure 65 shows the general nature of the change in the potential energy of interaction between molecules as a function of the distance between them. Actually, the molecules are in a state of rapid motion, and we can only speak of a certain average distance between them and a certain average potential energy. The mean distance depends on the density: the higher the density, the smaller the mean distance. It also depends on the temperature: the higher the temperature, the smaller the mean distance. This is due to the fact that the kinetic energy of molecules increases with temperature, and they approach closer to each other upon collisions. Consequently, the molecules spend a relatively large part of time at short distances from one another. It is clear that under these conditions, the expansion of a real gas without heat exchange must be accompanied by a change in its temperature.

Indeed, if the density and temperature of a gas are sufficiently high, the mean distance between molecules is less than r_0 . Figure 65 shows the values of the kinetic energy E , the potential energy U , and the total energy $E + U$. Apparently, in the case under consideration, a small increase in the volume, and hence a small decrease in the pressure, should lead to an increase in the temperature. If the density and temperature of the gas are such that the mean distance between molecules is larger than r_0 , a small increase in the volume, and hence a small decrease in the pressure, will lead to a decrease in the temperature. Such a change in temperature of a real gas under a very small adiabatic change in its volume and pressure is called the differential Joule-Thomson effect. In case of a significant change in the pressure (volume) small temperature differences should be summed up. This total effect is called the integral Joule-Thomson effect. This effect may involve an increase in the gas temperature (when the contribution of the differential effects with $\Delta T > 0$ exceeds the negative contribution with $\Delta T < 0$) or a decrease in the gas temperature.

Thorough experimental investigations of this phenomenon, which confirmed a variation of temperature for a steady-state flow of a gas through a porous plug were carried out in 1852-1862 by Joule and Thomson (later Lord Kelvin). The phenomenon discovered by them was called the Joule-Thomson (Joule-Kelvin) effect.

CALCULATION OF THE DIFFERENTIAL JOULE-THOMSON EFFECT. There is no direct heat exchange between gases in volumes V_1 and V_2 through the porous

plug, which is usually made of a material with a very low thermal conductivity. The entire system is thermally insulated. Hence, for a certain amount of a gas which occupied a volume ΔV_1 to the left of the plug and had an internal energy ΔU_1 , and which, after passing through the porous plug, occupies a volume ΔV_2 and has an internal energy ΔU_2 , the law of conservation of energy has the form

$$\Delta U_1 + p_1 \Delta V_1 = \Delta U_2 + p_2 \Delta V_2. \quad (33.1)$$

The quantities on the left- and right-hand sides of this relation are called the enthalpy of the gas under consideration. Hence, Eq. (33.1) indicates that the Joule-Thomson effect occurs at a constant enthalpy. For a certain mass of the gas, Eq. (33.1) assumes the form

$$H = U + pV = \text{const}, \quad (33.2)$$

where the notation introduced in (17.7) is used.

If we choose T and p as independent variables, we get from (33.2)

$$dH = \left(\frac{\partial H}{\partial T} \right)_p dT + \left(\frac{\partial H}{\partial p} \right)_T dp = 0. \quad (33.3)$$

Taking (23.30) into account, we can write

$$\left(\frac{\partial H}{\partial T} \right)_p = C_p, \quad \left(\frac{\partial H}{\partial p} \right)_T = V - T \left(\frac{\partial V}{\partial T} \right)_p. \quad (33.4)$$

Consequently, (33.3) yields

$$\left(\frac{\partial T}{\partial p} \right)_H = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T} \right)_p - V \right]. \quad (33.5)$$

This formula describes the differential **Joule-Thomson effect**.

For an ideal gas, $(\partial V / \partial T)_p = R/p = V/T$, and hence $(\partial T / \partial p)_H = 0$, the Joule-Thomson effect is not observed.

INTEGRAL EFFECT. If the difference between the pressures p_1 and p_2 on different sides of the plug is finite, the Joule-Thomson process can be represented as a sequence of quasistatic Joule-Thomson processes in each of which the pressure changes by an infinitely small value dp . For this



In a real gas, a permanent fight between attractive and repulsive forces takes place. If upon a certain change in pressure the mean energy of interaction between molecules decreases, the gas is heated, and if it increases, the gas is cooled. This determines the sign of the differential Joule-Thomson effect, which can be different at different pressures.

sequence of processes, we can write

$$T_2 - T_1 = \int_{p_1}^{p_2} \left(\frac{\partial T}{\partial p} \right)_H dp = \int_{p_1}^{p_2} \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T} \right)_p - V \right] dp. \quad (33.6)$$

Since the sequence of the quasistatic Joule-Thomson processes transforms the system from the same initial to the same final state, Eq. (33.6) gives the complete change in the temperature in a real Joule-Thomson process, i.e. is the formula for the integral effect.

JOULE-THOMSON EFFECT IN THE VAN DER WAALS GAS. In the general case, the calculation of the derivative $(\partial V/\partial T)_p$ is cumbersome, since the Van der Waals equation is a third-degree equation in V . For this reason, we shall confine ourselves to the case of a sufficiently rarefied Van der Waals gas, when in the virial representation (32.5) of this equation we can limit ourselves only to the terms which are linear in a and b , and take into account the first correction for the deviation of the gas from an ideal behaviour. Under these conditions, Eq. (32.5) assumes the form

$$\begin{aligned} V &= \frac{RT}{p} + \frac{1}{pV} (RTb - a) = \frac{RT}{p} + \frac{1}{RT} (RTb - a) \\ &= \frac{RT}{p} + b - \frac{a}{RT}, \end{aligned} \quad (33.7)$$

where in the correction term RT is substituted for pV in accordance with the equation for an ideal gas, since such a substitution introduces only those corrections which have higher order in a and b than the corrections taken into account in this equation. It follows from (33.7) that

$$\left(\frac{\partial V}{\partial T} \right)_p = \frac{R}{p} + \frac{a}{RT^2}. \quad (33.8)$$

Consequently, formula (33.5) for the differential effect assumes the form

$$\begin{aligned} \left(\frac{\partial T}{\partial p} \right)_H &= \frac{1}{C_p} \left(\frac{TR}{p} + \frac{Ta}{RT^2} - \frac{RT}{p} - b + \frac{a}{RT} \right) \\ &= \frac{1}{C_p} \left(\frac{2a}{RT} - b \right). \end{aligned} \quad (33.9)$$

This equation shows that at a sufficiently low temperature, $(\partial T/\partial p)_H > 0$, i.e. the gas is cooled upon expansion, while at a sufficiently high temperature, $(\partial T/\partial p)_H < 0$, i.e. the gas is heated upon expansion. Such a behaviour of the gas is in complete agreement with the physical sense of the Joule-Thomson effect. The temperature at which $(\partial T/\partial p)_H = 0$, i.e. the Joule-Thomson effect changes its sign, is called the inversion temperature:

$$T_{inv} = 2a/(Rb). \quad (33.10)$$

In order to calculate the integral Joule-Thomson effect for a Van der Waals gas, it is convenient to directly proceed from the constant enthalpy condition (33.2). Suppose that a gas has a volume V and V' before and after percolating through the porous plug. There are no limitations on the density of the gas in the initial state, while for the final state it is assumed that the gas is sufficiently rarefied and behaves as an ideal gas. The condition (33.2) then becomes

$$C_V T - a/V + pV = C_V T' + p'V' = C_V T' + RT', \quad (33.11)$$

where the unprimed quantities pertain to the initial state, and the primed quantities to the final state. It follows from the Van der Waals equation that

$$pV = \frac{RTV}{V-b} - \frac{a}{V} = RT + \frac{bRT}{V-b} - \frac{a}{V}. \quad (33.12)$$

Combining this expression with (33.11), we get

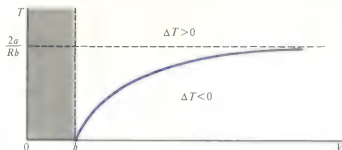
$$T' - T = \Delta T = \frac{1}{C_p} \left(RT \frac{b}{V-b} - \frac{2a}{V} \right), \quad (33.13)$$

where $C_p = C_V + R$. This formula describes the integral Joule-Thomson effect. The sign reversal of this effect occurs at the points for which $\Delta T = 0$, i.e.

$$RT \frac{b}{V-b} - \frac{2a}{V} = 0, \quad T = \frac{2a}{Rb} \left(1 - \frac{b}{V} \right). \quad (33.14)$$

The inversion curve for the integral Joule-Thomson effect for a Van der Waals gas is shown in Fig. 74. The inversion temperature for a sufficiently rarefied gas is equal to $2a/(Rb)$, which coincides with the inversion temperature for the differential effect, given by (33.10). With increasing density, the inversion temperature decreases. By definition, the

Fig. 74. The inversion curve of the Joule-Thomson effect for the Van der Waals gas



smallest possible volume for a Van der Waals gas is equal to b . However, we must bear in mind that when deriving the formulas, we assumed that the initial state was gaseous, and the inversion temperature is meaningless for other states of aggregation.

The shape of the inversion curve (Fig. 74), obtained for a Van der Waals gas, is typical of all real gases. This follows from the law of corresponding states. For most of gases, the inversion temperature is considerably higher than the room temperature, hence these gases are cooled in the Joule-Thomson process. Oxygen and nitrogen are examples of such gases. For some other gases such as hydrogen and helium, the inversion temperature is below the room temperature, and hence they are heated in the Joule-Thomson process.

LIQUEFACTION OF GASES. If a gas is below its critical temperature, it can be liquefied simply by compression. However, the critical temperature for most gases is very low. For example, the critical temperature of helium, hydrogen, nitrogen, and oxygen is 5.3, 33, 126.1, and 154.4 K respectively. Yet it is simpler and technically more important for storage to liquefy gases at atmospheric pressure. For this purpose, the gases must be liquefied at temperature below the critical, at which their saturated vapour pressure is equal to the atmospheric pressure. For the gases indicated above, this temperature is 4.4, 20.5, 77.4, and 90 K respectively.

It is not easy to attain such a low temperature. In order to decrease the temperature, a gas is cooled by using the Joule-Thomson process and adiabatic expansion.

The procedure of cooling a gas by using these methods is as follows. The gas is isothermally compressed up to several hundreds atmospheres at an attainable (e.g. room) temperature. After this, it is allowed to expand either in the Joule-Thomson process, or adiabatically. In both cases the gas is cooled. It is then used to cool the next portions of the

gas, compressed to a higher pressure. Consequently, the next portion of compressed gas has a lower temperature than in the preceding act of cooling. Hence, after expansion either as a result of the Joule-Thomson process or adiabatically, this portion of gas has a lower temperature than attained in the previous act. It is used to cool the next portion of the initial gas, and so on. In the long run, the temperature is lowered to the required value.

In real refrigerators, a combination of cooling processes is normally used. Besides, cooling is carried out quasicontinuously, i.e. a portion of gas cooled in the preceding stage is partially returned to the compression stage, and on its way cools the next portion of compressed gas, which then gets cooled as a result of the Joule-Thomson process or during adiabatic expansion. This method of cooling a gas through heat exchange between opposite gas flows is called the method of counterflow heat exchange.

A device where this process occurs is called a heat exchanger. The gas is cooled as a result of adiabatic expansion in a gas-expansion machine. A device where isothermal compression takes place is called a compressor. The Joule-Thomson processes and adiabatic expansion are technically combined so that the efficiency of liquefaction is maximum. It is often expedient to cool the gas in the initial compressed state to a sufficiently low temperature by another liquefied gas obtained in another machine. For example, in production of liquid helium, liquid hydrogen is used for preliminary cooling. The constructional details of machines and possible combinations of cooling methods are quite diverse and are beyond the scope of this book. Their description can be found in a low-temperature physics laboratory manual.

Liquefied gases can be used for direct cooling of other objects, since heat exchange in this case is sufficiently good. Upon a further decrease in temperature, liquid gases solidify (except He II). However, substances in the solid state cannot be used as cooling agents, since in this case heat exchange is ineffective. Taking into account the crystallization and boiling temperatures of the indicated gases, we can obtain the following temperature intervals by liquefaction of gases:

63.14-77.32 K (nitrogen)
 54.36-90.12 K (oxygen)
 14.04-20.39 K (hydrogen)
 0.7-4.21 K (helium)

In the first three cases the external pressure is equal to the atmospheric pressure. For liquid helium, 0.7 K is the lowest temperature which can be attained upon evacuation of liquid

?

1. How can we graphically explain the dependence of the sign of the differential Joule-Thomson effect on the gas pressure?
2. Which physical conditions in a gas correspond to the inversion point of the differential Joule-Thomson effect?
3. Prove qualitatively that for a given gas there exist pressure regions for which the integral Joule-Thomson effect may be either positive or negative, while there is pressure region where the effect can be both positive and negative, depending on the final pressure.

helium ^4He vapour. In this case the pressure is 0.293 Pa. A further decrease in temperature by lowering pressure is impossible because helium has a tendency to evaporate rapidly and no pumps are available to evacuate the helium vapour and decrease the pressure.

For attaining lower temperature, the magnetic cooling method is used. This method can be described as follows. There are substances whose molecules have a permanent magnetic moment. Such substances are called paramagnetics. When a paramagnetic is magnetized, the magnetic moments of molecules are reoriented along the magnetic field. This corresponds to a decrease in the potential energy of the magnetic moments of molecules in an external magnetic field. It is clear that as a result of magnetization, i.e. upon an ordering of molecules, the potential energy of interaction with the magnetic field decreases, and the entropy of the system drops (since we are talking about ordering).

Suppose that a certain paramagnetic is cooled to liquid helium temperature (say, to 0.7 K) by direct contact. The paramagnetic is then placed into a slowly increasing magnetic field and is adiabatically magnetized. The entropy of the system does not change during the reversible adiabatic slow process. However, the entropy associated with the orientation of molecules in the magnetic field decreases, and hence the entropy associated with the thermal motion increases. In other words, the paramagnetic gets heated. The magnetized paramagnetic is then brought in contact with liquid helium, as a result of which its temperature must drop to 0.7 K. After this, it is isolated from the liquid helium, and the external magnetic field is slowly reduced to zero. The paramagnetic is demagnetized, and the entropy associated with the orientation of magnetic moments increases, while the entropy associated with the thermal motion of molecules decreases. In other words, the paramagnetic is cooled below the initial temperature of 0.7 K.

In actual practice, however, there is no need to adiabatically heat the paramagnetic. This process has been described only to give a complete physical picture. It is enough to magnetize the paramagnetic in contact with liquid helium, after which it is isolated and is adiabatically demagnetized very slowly so that the process is accomplished reversibly.

Various paramagnetic salts are used for cooling. In particular, ammonium ferric alums are widely employed for this purpose.

With the help of magnetic cooling, a record low temperature of the order of 10^{-3} K has been attained. The

cooled salt can be used for cooling other materials brought in contact with it.

Many unusual properties are exhibited by materials at low temperatures. The most interesting of these properties, which are described in detail in Sec. 47, are observed in the case of He II.

PROPERTIES OF MATERIALS NEAR ABSOLUTE ZERO. Since the heat capacity C_V is positive, the internal energy U is a monotonic function of temperature. The internal energy decreases with temperature, and hence attains its minimum possible value at absolute zero. This applies to the system as a whole, as well as to its parts. Hence, the internal energy of all parts of the system attains its minimum value at 0 K, i.e. any part of the system is in its ground state with minimum energy.

It follows from the relation $\delta Q = T dS$ that the entropy of a substance decreases upon cooling. One can ask if the entropy tends to a certain definite value in this case. A positive answer to this question is given by the Nernst heat theorem which cannot be derived from the two laws of thermodynamics and is therefore sometimes called the third law of thermodynamics. Besides stating that the entropy tends to a certain limit as we approach absolute zero, this theorem also states that at 0 K all processes transferring a system from one equilibrium state to another take place without any change in entropy. The last statement means that at 0 K the entropy is independent of the parameters characterizing the state of the system (i.e. pressure, volume, etc.). The third law of thermodynamics was enunciated in 1906 by Nernst (1864-1941).

The numerical value of the entropy at 0 K is not fixed, but it is convenient to take it equal to zero. When defined in this way, it is called the absolute entropy. In any state of a system, its value is

$$S = \int_{T=0}^T \frac{\delta Q}{T}. \quad (33.15)$$

In this integral, the lower limit indicates the state at 0 K, while the upper limit, the state under investigation at a temperature T . The remaining parameters characterizing this state are not written in an explicit form.

The Nernst theorem has a number of important corollaries. First of all, it follows from this theorem that 0 K cannot be

!

As a system approaches the absolute zero of thermodynamic temperature, the internal energy of all parts of the system tends to its minimal value, and the entropy tends to a certain limit. Thus, all processes which transform the system from one equilibrium state to another at absolute zero must occur at a constant entropy.

The temperature of 0 K cannot be attained as a result of a finite number of operations.

attained as a result of a finite number of operations. This is evident, for example, from the analysis of magnetic cooling. Each adiabatic reversal of magnetization leads to a decrease in temperature. In this way, we can gradually approach 0 K. But since the entropies of the system in a magnetic field and without it become closer in value and tend to a common limit as we approach absolute zero, these steps gradually become shorter and shorter. Hence, after a sufficiently large number of magnetization reversals, we can in principle come infinitely close to absolute zero, but 0 K cannot be attained as a result of a finite number of such steps. Sometimes, the third law of thermodynamics is formulated as a statement about unattainability of 0 K in a finite number of operations.

It follows from the Nernst theorem that at 0 K heat capacities C_p and C_V are equal to zero. In order to verify this, it is sufficient to rewrite the expressions for the heat capacities on the basis of their definition $C = \delta Q/\delta T$ and formula $\delta Q = TdS$:

$$C = T \frac{\partial S}{\partial T} = \frac{\partial S}{\partial \ln T}, \quad (33.16)$$

where C may stand either for C_V or C_p , and accordingly the derivatives on the right-hand side are calculated either at a constant V , or at a constant p . Since $\ln T \rightarrow -\infty$ as $T \rightarrow 0$ K, and S tends to a certain limit, it follows from formula (33.16) that

$$C_V = 0, \quad C_p = 0 \quad \text{at} \quad T = 0 \text{ K}. \quad (33.17)$$

Let us now consider the temperature dependencies of the pressure and volume of the system at 0 K. The last two Maxwell thermodynamic relations (23.18) have the form

$$\begin{aligned} (\partial S/\partial V)_T &= (\partial p/\partial T)_V; \\ -(\partial S/\partial p)_T &= (\partial V/\partial T)_p. \end{aligned} \quad (33.18)$$

It follows from the Nernst theorem that at 0 K the left-hand sides of these relations are equal to zero. Consequently,

$$(\partial p/\partial T)_V = 0, \quad (\partial V/\partial T)_p = 0 \quad \text{at} \quad T = 0 \text{ K}, \quad (33.19)$$

i. e. at 0 K the pressure and the volume become independent of temperature. In other words, as we approach 0 K, the coefficient of pressure increase at constant volume and the coefficient of volume increase at constant pressure both tend to zero.



The sign of the differential Joule-Thomson effect may be different for different values of pressure and temperature. The sign of the integral Joule-Thomson effect may also be different depending on the range of variation of parameters for which it is calculated. Its sign is determined by the sign of the differential effect in the range of variation of parameters which make the main contribution to the integral effect.

Sec. 34. SURFACE TENSION

The mechanism of emergence of the surface tension is explained, and its quantitative characteristic is given. The equilibrium conditions at the interface between two media are considered. Capillary phenomena and the properties of surface-active materials are described.

$$F = \sigma S$$

FREE SURFACE ENERGY. The liquid state emerges when the potential energy of attraction between molecules exceeds (in magnitude) their kinetic energy. The repulsive forces between molecules in a liquid are sufficiently large to retain the molecules in the volume of the liquid. Thus, a liquid has a surface confining its volume. It is well known from geometry that for a given volume, the minimum surface is spherical.

The particles in a thin layer near the surface of a liquid are subjected to the forces acting from other molecules of the liquid. The resultant of these forces is directed inward normally to the surface (Fig. 75). As the surface increases, a certain number of molecules must go over from the bulk to the surface of the liquid. This can be done at the expense of work. If the formation of the surface is an isothermal process, the potential energy of the surface is equal to the energy spent in its formation and taken with the opposite sign. On the other hand (see Sec. 23), the role of potential energy in isothermal processes is played by the free energy F for which the following relation holds:

$$dF = -dA, \quad (34.1)$$

where dA is the work associated with the emergence of the free energy dF .

Since the surface is homogeneous, the free energy is obviously proportional to the area of the surface. Taking into account the above remarks and Eq. (34.1), we can write

$$F = \sigma S, \quad (34.2)$$

where σ is the free surface energy density.

SURFACE TENSION. Just as in mechanics a system strives to attain the state with the minimum potential energy, this being the only stable state of the system, in thermodynamics, a system under isothermal conditions endeavors to attain the state with the minimum free energy. Hence, the surface of a liquid tends to contract. This gives rise to forces which act along the surface and are called surface tension forces. In this respect, a liquid is identical to a thin rubber film stretched in all directions in the plane of the surface.

The presence of surface tension can be very effectively demonstrated with the help of soap films. For example, a wire frame immersed into a soap solution and taken out is



Fig. 75. The resultant of the forces acting on a molecule in the vicinity of the liquid surface

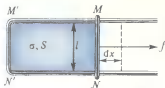


Fig. 76. To the calculation of the surface tension

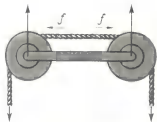


Fig. 77. Schematic diagram of forces leading to the emergence of the surface tension

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The free energy due to surface tension is proportional to the surface area of a body, i.e. to the square of its linear dimensions, while the weight is proportional to its mass, i.e. to the cube of linear dimensions. Hence, in the gravitational field of the Earth, surface tension is noticeable only for small volumes of a liquid, e.g. drops, and for small surfaces, for example, the liquid surfaces in capillaries.

covered by a soap film (Fig. 76). If one side of the frame, say, MN , can slide without friction along the wires MM' and NN' , the forces of surface tension will pull it toward $M'N'$, and the area of the film will contract. On the contrary, in order to increase the area of the soap film, we must apply a force f to MN . Upon a displacement of this wire by dx , the work $dA = f dx$ is performed, and the area of the soap film in this case changes by $dS = l dx$. Therefore, if we take into account Eq. (34.1.), Eq. (34.2) assumes the form

$$dF = 2\sigma dS = -f dx = -f dS/l, \quad (34.3)$$

where the factor 2 takes into account the fact that the film has two surfaces. The quantity $-f/(2l)$ is the force per unit length of MN for each of the film surfaces, acting toward the soap film. Numerically, this force is equal to the free surface energy density, since $1 \text{ J/m}^2 = 1 \text{ N/m}$. For this reason, the quantity σ is called the surface tension. It depends on the properties of the liquid and varies over a wide range. For most liquids, the surface tension has an order of magnitude from 10^{-2} to 10^{-1} N/m at 20°C . For example, the surface tension of ether, acetone, benzene, glycerin, and water is equal to 1.71×10^{-2} , 2.33×10^{-2} , 2.89×10^{-2} , 6.57×10^{-2} , and $7.27 \times 10^{-2} \text{ N/m}$ respectively. However, for mercury $\sigma = 0.465 \text{ N/m}$.

THE MECHANISM OF EMERGENCE OF SURFACE TENSION. The free energy characterized by σ is concentrated in a thin surface layer of a liquid. Consequently, the forces of surface tension also act in a thin surface layer only. In this respect, the thin surface layer is similar to a rubber membrane enveloping the liquid. The only difference is that the rubber membrane has a constant tension regardless of the changes in the liquid surface as a result of a change in the volume occupied by the liquid.

At first glance (see Fig. 75), it is not clear how the forces of surface tension acting along the surface emerge. In order to understand this, we must take into account the fact that in addition to these forces, some other forces act on the molecules of the surface layer, and prevent them from leaving the surface layer. The resultant of these forces is responsible for the surface tension (Fig. 77; a rope passing over two fixed pulleys is acted upon by forces f in the vertical direction, the tension f of the rope acts in the horizontal direction).

The surface tension depends on the properties of a substance in contact with the surface of the liquid. This is especially evident if we interpret σ as the free-energy density, since the material in contact with the liquid surface also acts on the surface layer molecules, and hence alters the forces

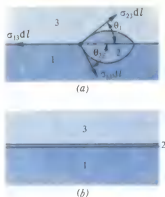


Fig. 78. Equilibrium conditions at the interface between two liquids

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Liquid drops have a spherical shape, since for a given volume the sphere has the minimum surface.

It is easier for molecules in a liquid to go over from the surface layer to the bulk of the liquid than in the opposite direction. For this reason, the concentration of molecules in the surface layer is lower than in the bulk. This causes the surface tension to appear.

pulling them inwards from the surface. This means that the surface tension σ changes. Consequently, when we speak of surface tension, we must specify not only the liquid we are dealing with but also the substance in contact with its surface, i.e. we must assign two subscripts to the symbol σ indicating the two bordering media, for example, σ_{12} , σ_{23} , etc. It is clear that the surface tension at the interface between two liquids must be lower than on the free surface. For instance, $\sigma = 0.0122$ N/m at the ether-water interface and 0.0336 N/m for water-benzene interface.

On the interface between a solid and a liquid, the surface tension also decreases in comparison with the free surface. For example, on the free surface of mercury $\sigma = 0.465$ N/m, while at the mercury-water interface it becomes equal to 0.427 N/m, and on the interface with alcohol, 0.399 N/m.

The values of σ given above correspond to room temperature.

DIRECT MANIFESTATIONS OF SURFACE TENSION. Since for a given fixed volume the sphere has the minimum volume, liquids assume spherical shape under zero-gravity condition. In the gravitational field of the Earth, only small drops assume spherical shape. This is due to the fact that the free surface energy decreases in proportion to the area of the surface, i.e. as the square of the linear dimensions of a drop, while the force of gravity acting on it decreases in proportion to its mass, i.e. as the cube of the linear dimensions. Therefore, with decreasing size the relative significance of the free surface energy increases, and for sufficiently small dimensions the drop assumes a shape close to spherical. Small mercury globules are another example illustrating surface tension. If we take two immiscible liquids of approximately identical densities and introduce a small amount of one of them into the other, the former will assume the shape of a sphere. In this case, the Archimedes buoyancy force balances the force of gravity, and surface tension is manifested in an almost pure form.

EQUILIBRIUM CONDITIONS AT THE INTERFACE BETWEEN TWO LIQUIDS. If a drop of a liquid is placed on the surface of another lighter liquid, two cases are possible (Fig. 78) depending on the relation between surface tensions. If dl denotes the element of length along the line of contact between the three media 1, 2, and 3, the surface tension forces acting on this element will be $\sigma_{12}dl$, $\sigma_{23}dl$, and $\sigma_{13}dl$. Note that dl is directed perpendicularly to the plane of the drawing. If $\sigma_{13} < \sigma_{23} + \sigma_{12}$, we will have the case of equilibrium shown in Fig. 78a. In the equilibrium state, the resultant of all forces acting on the element dl becomes equal

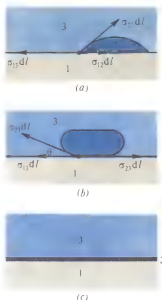


Fig. 79. Equilibrium conditions at the liquid-solid interface

to zero:

$$\sigma_{13} = \sigma_{23} \cos \theta_1 + \sigma_{12} \cos \theta_2, \quad \sigma_{23} \sin \theta_1 = \sigma_{12} \sin \theta_2. \quad (34.4)$$

This system of equations allows us to determine the angles θ_1 and θ_2 , which are called wetting angles.

If, however, $\sigma_{13} > \sigma_{23} + \sigma_{12}$, the equilibrium case indicated above is impossible, and the drop of liquid 2 will spread over the surface of liquid 1 in the form of a thin molecular layer (Fig. 78b).

EQUILIBRIUM CONDITIONS FOR THE LIQUID-SOLID INTERFACE. Two equilibrium cases are possible, shown in Fig. 79a, b. The equilibrium conditions in this case have the form

$$\sigma_{13} = \sigma_{23} \cos \theta + \sigma_{12} \quad \text{and} \quad \sigma_{23} \cos \theta + \sigma_{13} = \sigma_{12}. \quad (34.5)$$

If $\sigma_{13} > \sigma_{23} + \sigma_{12}$, the liquid spreads over the surface of the solid in the form of a molecular layer. In this case it is said to wet the surface of the solid. This is the case of a complete wetting (Fig. 79c). Figure 79a illustrates a partial wetting, while Fig. 79b shows a completely nonwetting liquid.

The shape of the surface of a liquid in contact with the vertical walls of the vessel containing it depends on whether or not the liquid wets the vessel walls. Figure 80a illustrates the case of wetting, and Fig. 80b shows the shape assumed by a nonwetting liquid.

Wetting and nonwetting effects create additional forces on a floating body, which either increase or decrease the buoyancy. If the liquid wets the solid (Fig. 81a), the surface tension acts against the buoyant force and tends to immerse the body into the liquid. On the other hand, if the liquid does not wet the solid, the surface tension is directed upwards and tends to push the body out of the liquid (Fig. 81b). These additional forces due to surface tension are normally small in comparison with the Archimedes buoyant force. However, in some situations these forces are significant. For example, if the density of a floating body only slightly exceeds the density of the liquid, and the line of its contact with the liquid surface is sufficiently long, it may happen that the body will not sink only due to the surface tension in the case of a nonwetting liquid. Some insects can run over the water surface and are not drowned due to the surface tension of water.

THE PRESSURE UNDER A CURVED SURFACE. If a surface is not flat, the surface tension leads to a pressure exerted by the surface layer on the deeper-lying layers. In order to calculate this pressure, let us consider a spherical soap bubble. The pressure p' inside the bubble, excessive in

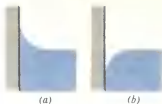


Fig. 80. The shape of the liquid surface near the vessel wall for a wetting (a) and nonwetting (b) liquid

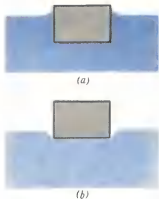


Fig. 81. Flotation of a body wetted (a) and nonwetted (b) by a liquid

comparison with the atmospheric pressure, is counterbalanced by the pressure from the bubble walls, caused by the surface tension. If the pressure inside the bubble increases, its radius receives an increment dr , and the work $4\pi r^2 p' dr$ accomplished in this case is converted into the free surface energy σdS of the bubble. It should be noted that the quantity dS is the total increase of the inner and outer surfaces of the soap bubble, i.e. $dS = 2d(4\pi r^2) = 2 \times 8\pi r dr$. According to the law of conservation of energy,

$$4\pi r^2 p' dr = 2\sigma \cdot 8\pi r dr, \quad (34.6)$$

whence

$$p' = 2 \cdot 2\sigma/r, \quad (34.7)$$

the pressure being created by the two curved surfaces of the soap bubble (inner and outer). One surface creates half of this pressure:

$$p = p'/2 = 2\sigma/r. \quad (34.8)$$

In the general case, the curvature of a surface is determined by two principal radii of curvature, r_1 and r_2 . In this case, the pressure is given by the relation

$$p = \sigma(1/r_1 + 1/r_2), \quad (34.9)$$

which is called the Laplace formula and which is given here without derivation. When $r_1 = r_2$, this formula becomes (34.8).

CAPILLARY EFFECTS. In the interaction between a liquid and a surface wall, the surface tension forces tend either to raise the level of the liquid (see Fig. 80a), or to lower it (Fig. 80b). If a liquid wets the walls of a tube, its level rises (Fig. 82a), while if it does not wet the walls, the level falls (Fig. 82b). The pressure of the column of liquid in a tube, raised to a height h , is compensated by the pressure created by the surface tension of the curved surface and directed upwards (Fig. 82a). Taking into account formula (34.8), we get

$$\rho gh = 2\sigma/R = 2\sigma \cos \theta/r, \quad (34.10)$$

where ρ is the density of the liquid, R is the radius of curvature of its surface, and r is the radius of the tube ($r = R \cos \theta$).

In a similar way we can calculate the depth to which the level of a nonwetting liquid drops (Fig. 82b) in a tube.

As the radius of the tube decreases, the height to which the

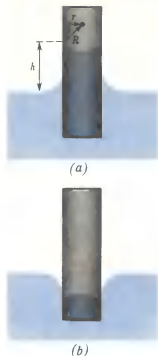


Fig. 82. Capillary phenomena

level of the nonwetting liquid rises increases and attains large values for sufficiently narrow tubes called capillaries (by analogy with very narrow blood vessels in animals and plants). For this reason, the effects associated with the interaction between the surface tension of a liquid and the tube walls are called capillary effects.

Liquids move in capillary tubes under the effect of the surface tension. These forces, however, may cause not only the motion of a liquid in a capillary, but also the motion of particles on the surface of a liquid. The most typical example of this effect is the "camphor dance".

During dissolution of camphor, the surface tension of water changes. For camphor crystals in the upper layers of water, dissolution occurs at different rates in different parts of the crystal surface. As a result, different forces of surface tension act on crystals from different sides. A small crystal sets in motion whose direction varies in accordance with the change in the distribution of the surface tension around it. The motion of the crystal causes certain hydrodynamic displacements of the liquid in the nearest layers and may even create ripples on the surface.

SURFACE-ACTIVE SUBSTANCES (SURFACTANTS). The surface energy tends to attain its minimum value. This can be done through a decrease in the surface area as well as the surface tension σ . Hence, if we add a liquid with a smaller tension to the liquid under consideration, the former will be mainly adsorbed in the surface layer, as a result of which the surface tension decreases. Such a substance is called a surfactant (for example, soap). Other materials increase the surface tension (e.g. solutions of sugar and various salts). Such materials are, on the contrary, concentrated beyond the surface layer of the liquid. If such a material is added to a solution containing surface-active substances, the latter are strongly pushed out to the surface. For example, the addition of salt to soap solution causes the expulsion of soap to the surface of the solution.

Example 34.1. Figure 76 shows a film formed by water. The approximate temperature dependence of the surface tension σ is given by the formula $\sigma = 7.3 \times 10^{-2} [1 + 0.5(1 - T/273)]$. The length of the movable wire is 5 mm.

Treating the process as isothermal at $T = 293$ K, find the force f , work A spent in stretching the film by $d = 1$ cm, and the change in the internal energy ΔU of the system upon increasing the film area by 1 cm^2 . Calculate the latent heat $L = (\partial Q / \partial s)_T$ of film formation, where s is the area of the film.

We denote the heat capacity of the film by $C = (\partial Q / \partial T)$,

and write the energy balance equation:

$$\delta Q = C dT + L ds. \quad (34.11)$$

The first law of thermodynamics in this case has the form

$$dU = C dT + (L + \sigma) ds. \quad (34.12)$$

The work and the force can be easily calculated:

$$f = 2\sigma l = 2 \times 7.3 \times 10^{-2} \left[1 + 0.5 \left(1 - \frac{293}{273} \right) \right] 5 \times 10^{-3} \text{ N} \\ = 0.7 \text{ mN};$$

$$A = fd = 7 \times 10^{-4} \times 10^{-2} \text{ J} = 7 \text{ } \mu\text{J},$$

where we took into account the fact that the film has two surfaces.

Using (34.11), we obtain the following formula for the entropy:

$$dS = \frac{\delta Q}{T} = \frac{C}{T} dT + \frac{L}{T} ds. \quad (34.13)$$

Since dS is a total differential, we can write

$$\frac{\partial}{\partial s} \left(\frac{C}{T} \right)_T = \frac{\partial}{\partial T} \left(\frac{L}{T} \right)_s, \quad (34.14)$$

?

whence

$$\frac{1}{T} \left(\frac{\partial C}{\partial s} \right)_T = - \frac{L}{T^2} + \frac{1}{T} \left(\frac{\partial L}{\partial T} \right)_s. \quad (34.15)$$

On the other hand, considering that dU in (34.12) is also a total differential, we get

$$\left(\frac{\partial C}{\partial s} \right)_T = \left(\frac{\partial L}{\partial T} \right)_s + \left(\frac{\partial \sigma}{\partial T} \right)_s. \quad (34.16)$$

The last two equations yield

$$L = -T \left(\frac{\partial \sigma}{\partial T} \right)_s. \quad (34.17)$$

Considering that $\partial \sigma / \partial T = [-7.3 \times 10^{-2} \times 0.5/273] \text{ J}/(\text{m}^2 \cdot \text{K})$, we obtain

$$L = \frac{293 \times 10^{-2} \times 7.3 \times 0.5}{273} \text{ J/m}^2 = 3.9 \times 10^{-2} \text{ J/m}^2.$$

1. Under which conditions is a dissolved substance concentrated either in the surface layer, or beyond it? Give examples supporting your answer.
2. Surface tension does not depend on the geometrical sizes of vessels and the volume of a liquid. But why is it manifested most clearly only in narrow tubes or in small drops?
3. Does the density of a liquid depend (in principle) on its amount under zero gravity conditions? In which way? Which factors must be taken into account in order to estimate the magnitude of this effect?

Since L is positive, the film gets cooled as the area of the surface increases.

According to (34.12), the change in the internal energy at $T = \text{const}$ is

$$\Delta U = \int_{s_0}^s (L + \sigma) ds = (L + \sigma) \Delta s, \quad (34.18)$$

since L and σ are independent of s . Considering that

$$\begin{aligned} \sigma(293) &= 7.3 \times 10^{-2} \left[1 + 0.5 \left(1 - \frac{293}{273} \right) \right] \text{ N/m} \\ &= 7 \times 10^{-2} \text{ N/m} = 7 \times 10^{-2} \text{ J/m}^2, \end{aligned}$$

and using (34.18), we get

$$\Delta U = (3.9 \times 10^{-2} + 7 \times 10^{-2}) \times 0.5 \times 10^{-4} \text{ J} = 5.45 \text{ } \mu\text{J}.$$

Example 34.2. Assuming the initial area of the film (see Example 34.1) to be 0.5 cm^2 and its initial thickness as $1 \text{ } \mu\text{m}$, find the change in the entropy of the film upon a 2 cm^2 increase in its area at 273 K , and the change in the entropy caused by the temperature increase from 273 to 293 K for a constant area. Find the change in the film temperature accompanying an adiabatic increase of its surface by 1 cm^2 . The initial data are the same as in the previous example.

The change in the entropy can be found from formula (34.13). Since the volume of the film is

$$V = 10^{-6} \times 0.5 \times 10^{-4} \text{ m}^3 = 0.5 \times 10^{-10} \text{ m}^3 = \text{const},$$

its heat capacity (see (34.13)) is equal to

$$\begin{aligned} C &= 0.5 \times 10^{-10} \times 4.18 \times 10^3 \times 10^3 \text{ J/K} = 2.09 \times 10^{-4} \text{ J/K} \\ &= \text{const}. \end{aligned}$$

Integrating (34.13), we find

$$S - S_0 = C \ln \frac{T}{T_0} - \left(\frac{\partial \sigma}{\partial T} \right)_s (s - s_0), \quad (34.19)$$

where we have taken into account relation (34.17).

When the temperature changes at a constant surface area, we get

$$\begin{aligned} (\Delta S)_s &= C \ln \frac{T}{T_0} = 2.09 \times 10^{-4} \ln \frac{293}{273} \frac{\text{J}}{\text{K}} \\ &= 1.4776 \times 10^{-5} \text{ J/K}. \end{aligned}$$

If the area changes by $\Delta s = 2 \times 10^{-4} \text{ m}^2$ at a constant temperature, we obtain

$$(\Delta S)_T = - \left(\frac{\partial \sigma}{\partial T} \right) \Delta s = \frac{+ 7.3 \times 10^{-2} \times 0.5 \times 2 \times 10^{-4} \text{ J}}{273 \text{ K}}$$

$$= 2.67 \times 10^{-8} \text{ J/K}.$$

Proceeding from (34.11), we find for the adiabatic increase in the area ($\delta Q = 0$)

$$dT = - \frac{L}{C} ds = \frac{T}{C} \left(\frac{\partial \sigma}{\partial T} \right) ds, \quad (34.20)$$

whence

$$\Delta T = \frac{- 293 \times 1.33 \times 10^{-4} \times 2 \times 10^{-4}}{2.09 \times 10^{-4}} \text{ K} = - 0.038 \text{ K}.$$

Example 34.3. Find the radius of a liquid drop emerging from a narrow vertical tube of radius r . Assume that the drop has a spherical shape when it breaks away from the tube.

The drop is held at the tube by the surface tension acting along the circumference $2\pi r$. Hence, the force is equal to $2\pi r\sigma$. The weight of a suspended drop of radius R is equal to $4\pi R^3 \rho g/3$, where ρ is the density of the liquid. The drop tears away when $4\pi R^3 \rho g/3 = 2\pi r\sigma$, whence

$$R = [3r\sigma/(2\rho g)]^{1/3}.$$

If, for example, we assume that $\sigma = 7.5 \times 10^{-2} \text{ N/m}$ for water we get for $r = 10^{-3} \text{ m}$

$$R = 2.26 \times 10^{-3} \text{ m}.$$

Sec. 35. EVAPORATION AND BOILING OF LIQUIDS

The dependence of the saturated vapour pressure on the curvature of the surface and the role of this dependence in evaporation and boiling is investigated. The conditions for the existence of superheated liquid and supercooled vapour and their applications are considered.

EVAPORATION. The forces acting in the surface layer and near the surface of a liquid determine the existence of the surface and do not allow the molecules to leave the volume of the liquid. Due to thermal motion, a certain part of molecules have sufficiently high velocities to overcome the forces confining them in the liquid and to leave it. This phenomenon is called evaporation. It is observed at any temperature, but its intensity increases with temperature.

DYNAMIC EQUILIBRIUM. VAPOUR-LIQUID SYSTEM. If the molecules which have left a liquid are removed from the

Table 3
Saturated Vapour Pressure for Some Substances at 20° C

Substance	p , kPa	Substance	p , kPa
Acetone	24.0	Mercury	1.63×10^{-4}
Benzene	10.0	Toluene	2.93
Water	2.34	Chloroform	21.3
Methyl alcohol	12.9	Ethyl alcohol	5.87

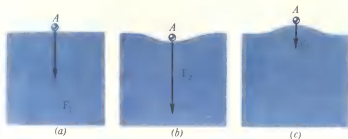
space near the surface of the liquid, the entire liquid will evaporate in the long run. However, if the molecules which have left the liquid are not removed but are kept in a closed volume near the liquid surface, the process develops in a different way. The molecules leaving the liquid form its vapour. Vapour molecules which get into the region near the liquid surface are pulled into the liquid by the forces of attraction. Thus, the evaporation rate decreases. A further increase in the vapour density leads to a state in which the number of molecules leaving a liquid during a certain time is equal to the number of molecules returning to the liquid during the same time. Thus, a state of dynamic equilibrium sets in. The vapour which is in dynamic equilibrium with its liquid is called the saturated vapour (see Sec. 30).

It is clear from what has been said above that with increasing temperature, the density (and hence the saturated vapour pressure) increases (Tables 3 and 4), as was shown by an analysis of the isotherms of a real gas. As the density of saturated vapour increases, the surface tension of the liquid decreases, since the forces directed inwards diminish due to an increase of the oppositely directed forces exerted by the saturated vapour. It also follows from the above arguments that with increasing temperature the latent heat of evaporation decreases. At the critical temperature, the density of the saturated vapour becomes equal to the density of the liquid, and the difference between them vanishes. This means that the interface between the liquid and the vapour

Table 4
Temperature Dependence of the Saturated Vapour Pressure for Water

t , °C	-5	-3	-1	0	1	3	5	9	15	20	25
p , kPa	0.401	0.463	0.563	0.611	0.656	0.757	0.872	1.148	1.704	2.337	3.168

Fig. 83. Schematic diagram illustrating the dependence of the saturated vapour pressure on the shape of the liquid surface



disappears, and at the critical temperature, the latent heat of evaporation and the surface tension become equal to zero.

In the strict sense of the word, a vapour is not a gas. A gas is the state of aggregation of a substance at a certain pressure and temperature, while the vapour is not a state of aggregation, because at a given temperature and pressure the state of aggregation of the corresponding substance is liquid. For this reason, the behaviour of vapour differs from the behaviour of gas. For one, in ideal gases the pressure is exactly inversely proportional to the volume, while in real gases this dependence holds with a sufficiently high degree of accuracy. However, for nearly-saturated vapour the pressure changes with the volume insignificantly and for saturated vapours does not change at all. Gas laws can be applied to unsaturated vapours to a rough approximation. But if a vapour is far from saturation, it can be described by the gas laws to a very good approximation.

SATURATED VAPOUR PRESSURE NEAR THE CURVED SURFACE OF A LIQUID. At the curved surface of a liquid, the pressure of its saturated vapour differs from that at a flat surface. In order to investigate the nature of this dependence, it is necessary to consider the conditions of dynamic equilibrium between the vapour and the liquid. In their physical content, they are similar to the conditions at a flat surface, under which the molecular intensities of transition from liquid to gas and from gas to liquid are equal. However, in the case of a curved surface, the intensity of the molecular exchange depends on the curvature of the surface. The calculation of this dependence allows us to determine the saturated vapour pressure near the curved surface. Figure 83 shows different types of curved surfaces (letter *A* denotes a molecule at the surface of a liquid, attracted by liquid molecules). Clearly, in case *b* this force is greater, and in case *c* smaller than for a flat surface (*a*). Hence, in case *b*, it is more difficult for liquid molecules to leave the liquid, while vapour molecules are pulled towards the liquid more

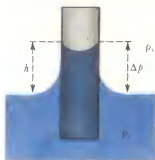


Fig. 84. To the calculation of the saturated vapour pressure above the curved surface

intensely than in case *a*. This means that in the case of a concave surface, the saturated vapour pressure is lower than at a flat surface. A similar reasoning shows that the saturated vapour pressure is higher in case *c* than in case *a*.

There is one more reason which makes the dependence of saturated vapour pressure on the curvature still stronger. In case *b*, the pressure due to surface tension is directed away from the liquid. As a result, the pressure inside the liquid near its surface becomes lower, the number of collisions between particles becomes smaller, which causes a decrease in the number of particles leaving the liquid, i.e. lowers the SVP near the concave surface still further. In case *c* similar causes have an opposite effect and increase the SVP near the convex surface.

In order to derive a relation connecting the change Δp in the SVP with the curvature of the surface, let us examine Fig. 84. If a tube and a liquid are contained in a closed vessel, the space above the liquid will be filled with its saturated vapour. The height h of the column of liquid in a capillary tube and the radius R of curvature of the liquid surface in the capillary depend on the surface tension, density of the liquid and its saturated vapour. At the surface of the liquid, the pressure inside the capillary tube is equal to the pressure outside it. The saturated vapour pressure at the height h is also the same in all parts of the vessel. If the opposite were true, horizontal flows of saturated vapour would appear. For this process to be steady-state, the appropriate flows would appear in the liquid, closing the lines of circulation of substance. In this case we should assume that at the same temperature, the nature of the liquid-vapour dynamic equilibrium in different parts of a flat surface is different (see Sec. 34). But this is in contradiction with the pattern of dynamic equilibrium described above.

Denoting by p_h the saturated vapour pressure at a height h , we can write

$$p_0 = p_h + \rho_v g h, \quad (35.1a)$$

$$p_0 = p_h - 2\sigma/R + \rho_l g h, \quad (35.1b)$$

where ρ_l and ρ_v are the densities of the liquid and saturated vapour. Equation (35.1a) expresses the pressure difference between the levels under consideration in vapour, while (35.1b) is the similar relation for liquid. The term $-2\sigma/R$ takes into account the difference in pressure on different sides of the curved surface of liquid. Equating the expressions (35.1a) and (35.1b) for p_0 we find

$$g h = 2\sigma / [R(\rho_l - \rho_v)]. \quad (35.2)$$

From Eq. (35.1a) we get

$$\Delta p = p_0 - p_h = \rho_v gh = 2\sigma\rho_v / [R(p_0 - p_v)], \quad (35.3)$$

where for gh we have substituted its expression (35.2).

This expression is called the Thomson formula. In formula (35.1a) we have assumed that the density of saturated vapour does not change with height. In most cases, this assumption holds quite well. If necessary, we can use the barometric formula (10.13) in order to take into account the effect of variation of the saturated vapour density with height.

BOILING. When a liquid is heated to a temperature at which its saturated vapour pressure becomes equal to the atmospheric pressure, the equilibrium between the liquid and its saturated vapour sets in. If additional amount of heat is supplied to the liquid, a certain portion of the liquid immediately evaporates. Theoretically, the lowest pressure in the liquid is observed in its upper layers, hence the liquid must vaporize first of all in the upper layers. Actually, however, the difference in pressures between various layers of the liquid is insignificant in comparison with the pressure itself, since 10^5 Pa correspond to the pressure of a 10 m thick layer of water. Besides, the liquid is usually heated from below. These two circumstances ensure an intense vaporization of liquid over the entire volume. This process is called boiling. The boiling point is the temperature at which the saturated vapour pressure becomes equal to the external atmospheric pressure. The boiling point rises with increasing pressure and falls with decreasing pressure. In a hermetically closed vessel, water can be heated to a temperature considerably higher than 100°C without boiling. This is used in everyday life when we cook food with the help of a pressure cooker. On the other hand, we can cause boiling at room temperature if we lower the pressure above the water surface, say, by pumping out the air from a closed vessel containing the liquid.

Thus, strictly speaking, at different levels in a liquid boiling occurs at different temperatures, and there is no definite boiling point for a liquid. But the saturated vapour above the surface of a boiling liquid has a definite temperature. This temperature does not depend on the nature of boiling at various depths and is determined by the external pressure alone. It is this temperature of the saturated vapour above the surface of a boiling liquid which is meant when we speak of a boiling point.

SUPERHEATED LIQUID. Now, we can explain the existence of a superheated liquid (see Sec. 32). If a liquid



An ion becomes a nucleus for condensation because the energy of its electric field decreases upon the formation and growth of a water drop around it.

The temperature dependence of the density and pressure of saturated vapour and the dependence of the boiling point on pressure are determined by the physical content of dynamic equilibrium. As the temperature increases, the dynamic equilibrium is maintained by increasing the saturated vapour pressure. If the pressure increases, the equilibrium is ensured by increasing the temperature.

containing no impurities or vapour bubbles is heated to the boiling point, vapour bubbles tend to form inside it. But as soon as such a bubble appears inside the liquid, the vapour inside the bubble, being saturated with respect to flat surface, is oversaturated with respect to concave surface confining this bubble. For this reason, the vapour in the bubble immediately condenses and the bubble disappears. This process is facilitated by an increase in pressure on the bubble from the concave surface of the liquid confining the bubble under consideration. This pressure also strives to break the vapour bubble formed.

Boiling starts if we introduce into the liquid something which would ensure the formation of vapour bubbles which from the very outset would have a sufficiently large radius so that the vapour inside the bubble is not too much supersaturated and the pressure from the bubble walls is not very high. This "something" can be, for example, chalk powder. Individual particles of the powder are the "nuclei" around which vapour bubbles are formed. Thus, if we drop a pinch of chalk into superheated water, we will cause vigorous boiling resembling an explosion. Another cause of bubble formation in a superheated liquid can be, for example, ions. This effect is used for tracing charged particles.

The maximum allowed superheating of a liquid can be estimated as follows. First of all, we must set the maximum radii R of the bubbles which may be formed around a nucleating centre in the liquid. From formula (35.3) we find the pressure required by this vapour to be saturated inside a bubble. In this case, since the density of saturated vapour at the boiling point is much lower than the density of the liquid, we can use this formula in the form $\Delta p = 2\sigma\rho_v/(Rp_l)$. Considering that $V_2 \ll V_1$, we find the permissible superheating from the Clausius-Clapeyron equation:

$$\Delta T = TV_1 \Delta p/L.$$

Substituting into this formula the values of the quantities taken from the tables, we find that $\Delta T \approx 0.5$ K for $R = 0.5 \cdot 10^{-7}$ m. Similarly, we can estimate the elevation of the boiling point with depth:

$$\Delta T = TV_1 \Delta p/L = V_1 p_1 T g \Delta h/L.$$

Hence, it follows that $\Delta T/\Delta h \approx 0.03$ K/cm. In other words, the boiling point at a depth of 10 cm from the surface in a kettle is about 0.3 K higher than at the surface.

BUBBLE CHAMBERS. If a charged particle flies through a superheated liquid, it ionizes the atoms of the liquid on its

path. These ionized atoms become the nucleating centres around which bubbles of saturated vapour are formed. In other words, the superheated liquid locally boils along the trajectory of a charged particle, owing to which the trajectory becomes visible and can be photographed.

Such photographs make it possible to study the motion of particles in various fields, their interaction, and so on. Usually, in experimental investigations of elementary particles liquid hydrogen is used. The above description explains the name "bubble chamber" given to this type of instruments for investigating the trajectories of charged particles. They play an important role in the elementary particle research. Bubble chambers helped to detect the majority of new particles and to make many other important discoveries.

SUPERCOOLED VAPOUR. A saturated vapour at a certain temperature is supersaturated with respect to a lower temperature. For this reason, a part of this vapour becomes liquid when the temperature is decreased. This phenomenon is called condensation. Under normal conditions, water vapour condenses in the entire volume of vapour in the form of very small droplets or mist. However, if the air containing saturated vapour is sufficiently well purified, its cooling will not lead to a condensation of the vapour, and a metastable state, called supercooled vapour, appears (see Sec. 32).

Small droplets of liquid are formed upon cooling a saturated vapour. However, they cannot exist infinitely long since the saturated vapour in which they are formed is unsaturated for the convex surface of the drops (see Fig. 83c). Hence the liquid of the drops immediately evaporates, and the drops disappear. Before the condensation starts, it must be ensured that liquid drops of sufficiently large radius can be formed so that the vapour would not be highly unsaturated for them. For this purpose, condensation nuclei must be present. In this respect, the situation is quite similar to that with a superheated liquid. Such nuclei can be, for example, ions, specks of dust, microbes, etc.

WILSON CLOUD CHAMBER. In a supercooled vapour a charged particle ionizes vapour molecules along its track. The ions become condensation sites around which liquid drops are formed. Owing to this, the trajectory of the particle becomes clouded and visible. This makes it possible to investigate charged particles, their interaction, and so on. Such an apparatus is called the Wilson cloud chamber, and it has played an important role in scientific investigations of elementary particles.

Why do ions become condensation nuclei? This is stipulated by the balance between the energy of condensation,

the surface energy, and the Coulomb energy. Water molecules have a large dipole moment. They surround a charged ion, being oriented with respect to it so that their dipoles turn to the ion with the opposite charge. An aggregate formed as a result of this process acts on surrounding particles as an ionic charge, causing another layer of molecules to join it. Thus, a growing drop of water is formed. The energy of this drop depends on its radius and consists of three components: the surface energy $E_{\text{sur}} = 4\pi r^2 \sigma$, where σ is the surface tension, the electric energy of the Coulomb field of the drop $E_{\text{el}} = q^2 / (4\pi \epsilon_0 r)$ (q is the charge of the ion and ϵ_0 is the electric constant), and $E_{\text{lat}} = -(4/3)\pi r^3 \rho L$ the energy due to the latent heat of condensation, where ρ is the density of the substance forming the drop and L the latent heat of condensation.

The total energy is

$$E = 4\pi r^2 \sigma + q^2 / (4\pi \epsilon_0 r) - (4/3)\pi r^3 \rho L.$$

The behaviour of a drop is determined by the changes in its energy during its growth, as the mass δm is added to it. If the energy increases, the drop cannot grow. The growth of the drop is possible only provided that $(\delta E / \delta m) < 0$. Considering that $\delta m = 4\pi r^2 \rho \delta r$, we obtain

$$\frac{\delta E}{\delta m} = \frac{\delta E}{\delta r} \frac{\delta r}{\delta m} = \frac{2\sigma}{\rho r} - \frac{q^2}{16\pi^2 \epsilon_0 \rho r^4} - L.$$

It can be seen that in the absence of an ion ($q=0$), the conditions are unfavourable for condensation, since for small r the first term on the right-hand side is large. The radii r_0 of nuclei must be very large to ensure that $[2\sigma/(\rho r_0)] < L$. The presence of an ion radically changes the situation. For small r , the negative term $-q^2/(16\pi^2 \epsilon_0 \rho r^4)$ is modulo sufficiently large, which makes condensation advantageous. The electric energy compensates the action of the surface energy preventing condensation if the radius of the drop satisfies the condition $2\sigma/(\rho r) = q^2/(16\pi^2 \epsilon_0 \rho r^4)$, i.e. for $r = [q^2/(32\pi^2 \epsilon_0 \sigma)]^{1/3}$.

For singly charged ions $q=e$ and the value of r is of the order of several angstroms. This means that the appearance of an ion has created highly favourable conditions for the formation of condensation sites.

Example 35.1. Find the molar heat of evaporation of a liquid at temperature T and saturated vapour pressure p , assuming that the liquid and its saturated vapour obey the

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The density and pressure of saturated vapour increase with temperature, while the surface tension and latent heat of evaporation decrease. The saturated vapour pressure above a concave surface is lower, and above a convex surface is higher than the pressure above a flat surface.

Van der Waals equation with given a and b , and the temperature T is far from critical (this allows us to take the molar gas constant for R).

Applying the first law of thermodynamics to the process of evaporation, we get

$$L = U_v - U_l + p(V_v - V_l), \quad (35.4)$$

where U_v and U_l are the internal energies of the vapour and the liquid, $p(V_v - V_l)$ is the work performed during evaporation against a constant external pressure p . According to the Van der Waals equation, the difference in internal energies is equal to

$$U_v - U_l = a/V_l - a/V_v,$$

and hence

$$\begin{aligned} L &= a(1/V_l - 1/V_v) + p(V_l - V_v) \\ &= V_v [RT/(V_v - b) - 2a/V_v^2] - V_l [RT/(V_l - b) - 2a/V_l^2]. \end{aligned} \quad (35.5)$$

Example 35.2. Find the rate of evaporation of a liquid, i.e. the ratio of the mass of the liquid converted into vapour to the interval of time and the area of the surface from which evaporation occurred, if the saturated vapour pressure and temperature of the liquid are known.

In dynamic equilibrium between vapour and liquid, the evaporation rate is equal to the rate of condensation. In saturated vapour, the velocities of molecules obey Maxwell's distribution law, and hence, according to formula (8.32), the evaporation rate for the liquid is equal to

$$I_m = mv = n_0 m [kT/(2\pi m)]^{1/2}, \quad (35.6)$$

where m , n_0 , and T are the mass of a molecule, the molecular concentration, and the temperature respectively.

Considering that $n_0 = p_s/(kT)$, we get

$$I_m = p_s [m/(2\pi kT)]^{1/2} = p_s [M/(2\pi RT)]^{1/2}, \quad (35.7)$$

where $M = mN_A$ is the molar mass of the vapour.

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1. What is the difference between the properties of a vapour and a gas? Under which conditions can the gas laws be applied to vapours?
2. What is the mechanism of formation of a supercooled vapour and a superheated liquid?

Sec. 36. STRUCTURE OF LIQUIDS. LIQUID CRYSTALS

The pair distribution function is used to characterize the short-range and long-range orders and to calculate the potential energy of intermolecular interaction. The dependence of the properties of a liquid on its molecular structure is analyzed. Basic properties and applications of liquid crystals are considered.

PAIR DISTRIBUTION FUNCTION. Molecules in gases are distributed quite randomly in space. A gas may serve as an example of a structureless formation. Solids illustrate the opposite case, since their atoms are located at quite definite points in space, which are called lattice sites. Clearly, crystalline solids have a definite internal structure. What is the position of liquids in this respect?

Initially, it was assumed that liquids are similar to gases in their structure, i.e. are structureless formations. With this approach, a liquid was simply considered a very dense gas. Experiments showed, however, that this is not true. Essentially, these experiments consist in the following. If a crystalline solid is exposed to X-rays, the pattern formed by the rays scattered by the solid has a certain order. This order is sufficient to draw definite conclusion about the structure of the crystal lattice. In other words, the pattern of the scattered X-ray radiation reflects the structure of the crystal lattice of a solid.

When X-rays are passed through a gas, the analysis of scattered radiation does not reveal any ordering. It can thus be concluded that gases are structureless formations. However, when X-rays are passed through a liquid, the scattered X-ray radiation is not as ordered as in the case of solids but still not as random as in the case of gases. Hence we can state that liquids have a structure which is not pronounced as clearly as in solids, but which differs from structureless gases. In their internal structure, liquids occupy an intermediate place between gases and solids. While considering some problems, it turned out to be more convenient to represent a liquid as a disordered solid in a certain sense.

For example, one of such approaches treats a liquid as a crystal in which a part of cells is not filled.

A quantitative characteristic of ordering in a structure is a pair distribution function $g(r)$ defined in the following way. Suppose that a certain hypothetical observer is at the site of some molecule and observes the mean density of other molecules in various small regions of the space, characterized by the radius vector r . This density distribution is described by the function $g(r)$. If we consider a solid, the density of molecules in it differs from zero only at the lattice sites.

For example, if we select a direction passing through the lattice points, the distribution function $g(r)$ along this

$$U \sim r^2 g(r)$$

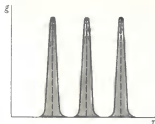


Fig. 85. Pair distribution function for a crystal

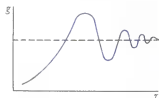


Fig. 86. Pair distribution function for liquids

direction has the form depicted in Fig. 85. The peaks correspond to the lattice sites, and the shape of curves in the vicinity of the peaks is Gaussian, since an atom is not fixed precisely at the lattice point but moves in the vicinity of this point. Obviously, the function $g(r)$ for a crystal depends not only on the magnitude of the vector r but also on its direction. In some other direction, the peaks are separated by different distances from each other and from the reference point. In an ideal gas, the distribution of molecules is uniform in all directions and at all distances from the reference point, i.e. for gases $g(r) = \text{const.}$ Experimental and theoretical investigations have shown that the pair distribution function for liquids is isotropic, but depends on the distance (Fig. 86). The density $g(r)$ oscillates about the mean density, and at large distances becomes equal to the mean density. This indicates that molecules in a liquid are distributed not as randomly as in a gas, although not as regularly as in a solid.

When we spoke of the mean density, we meant an averaging over time. Naturally, this definition can be reformulated on the basis of the ergodic hypothesis about the ensemble average. Let us fix the positions of all the molecules at a certain instant of time and consider various pairs of molecules. We calculate the total number of pairs whose separation lies between r and $r + dr$ for various values of r and divide it by the total number of pairs and dr . This relative number of molecules for different values of r will give, on a certain scale, the pair distribution function $g(r)$. Consequently, different separations of molecules in a liquid are not equally probable. This statement is just the quantitative formulation of the idea that a liquid has an internal structure (we mean short-range ordering).

The following rough analogy may help in proving the existence of an internal structure in a liquid. If we must put a small number of jars on a large shelf in a cupboard, there is no need to care about their relative positions so that they could be placed on the shelf. If, however, the number of jars is large, so that they can hardly be placed on the shelf, that is another matter. It is impossible to place the jars at random, and we must find some way which would ensure the maximum saving of space. The jars arranged in this way form a definite structure. Although the distribution of molecules in a liquid naturally differs from the arrangement of jars on a shelf, we can still use purely geometrical considerations about possible mutual positions of molecules to obtain the curves for $g(r)$ similar to those shown in Fig. 86.

CALCULATION OF POTENTIAL ENERGY. The importance of the pair distribution function lies in that it can be used to calculate the potential energy of interaction if we know the interaction potential $U(r)$ (see Fig. 65). The number of pairs of molecules separated by the distance r is proportional to $r^2 g(r)$, and hence the potential energy of interaction is proportional to the integral

$$\int_0^\infty r^2 g(r) U(r) dr. \quad (36.1)$$

If $g(r)$ and $U(r)$ are known as functions of density and pressure, all equilibrium properties of the liquid can be determined.

DEPENDENCE OF PROPERTIES OF A LIQUID ON MOLECULAR STRUCTURE. Since molecules in a liquid are close to each other, their internal structure and properties considerably influence the properties of the liquid. For example, the presence of constant dipole moments in molecules and their mutual orientation make different mutual orientations of molecules inequivalent. The shape of molecules considerably affects their mutual motion. For example, long molecules move with respect to each other not in the same way as spherical molecules do, and so on. This makes the description of the liquid state still more complicated.

LIQUID CRYSTALS. Thus, a liquid has a definite structure, though it is not as regular as the crystalline structure of a solid. However, there are many cases when liquids have more ordered structure than simply a structure with short-range order. It turns out that for many substances, especially organic materials, we cannot treat the transition from the solid to the liquid state as a single transition. For such materials this transition consists of a sequence of transitions in each of which the state and structure of the substance changes, and it is impossible to state that it is either in the liquid or in the solid state. The mechanical properties and structure of substances in such intermediate states lie between the solid and liquid states. A substance in the intermediate states is called liquid crystal.

TYPES OF LIQUID CRYSTALS. Liquids are characterized by the absence of any spatial ordering and anisotropy of their properties. The most significant property of the crystalline structure of solids is its three-dimensional ordering. Liquid crystals exhibit $\mu\mu\mu$ ordering which is intermediate between those of solids and liquids and which results in corresponding

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The existence of pair distribution function for liquids indicates a short-range order in them.

In theoretical studies of some phenomena in liquids, it is sometimes expedient to take the model of a solid rather than the model of a gas as a first approximation.

In their structure, liquids occupy an intermediate position between gases and solids: the arrangement of molecules in a liquid is not as regular as the structure of solids, but we cannot say that it is irregular at all, like gases.



Fig. 87. Smectic structure of the A type. The molecules in liquid layers are oriented on the average along the normal to the surface



Fig. 88. Smectic structure of the C type. The molecules in liquid layers are oriented at an angle to the surface of layers

anisotropy of their properties. Accordingly, liquid crystals can be divided into two groups. The first group of liquid crystals called smectics is characterized by a one-dimensional spatial ordering. Smectic liquid can be represented as consisting of parallel layers, which regularly alternate and differ from each other in their structural ordering. The second group of liquid crystals, called nematics, does not have spatial ordering and is characterized by orientational ordering of their molecules. The molecules of nematics are strongly elongated, and orientational ordering appears because of the preferential orientation of these long molecules. The molecules of smectics are also elongated. Hence, we can say that from the molecular point of view, a peculiar feature of liquid crystals is the elongated shape of their molecules, leading to anisotropy of their properties.

SMECTICS. There are three types of smectics. Let us denote them by A, B, and C. In A- and C-type smectics, the layers of liquid behave as a two-dimensional liquid, for which the distribution of centres of mass of the molecules is described by a binary function. In B-type smectics, the layers of liquid are closer in their properties to a two-dimensional solid. Within the layers, periodicity and rigidity typical of solids are observed. Owing to this, in particular, within each layer the diffraction of X-rays by solid-state ordering is observed. In contrast to the A- and C-type smectics in which the layers, as a rule, are curved, the layers of the B-type smectics are flat.

The thickness of the layers in A-type smectics is close to the length of molecules directed on the average perpendicularly to the boundary surface between the layers (Fig. 87). The local properties of the system of layers are axially symmetric with respect to the rotation axis, which is normal to the boundary surface between the layers, both directions of the normal being equivalent. Hence, it follows that from the point of view of optics, A-type smectics exhibit the properties of uniaxial crystal.

The thickness of the layers in C-type smectics is less than the length of molecules, and it is natural to assume that the molecules in these liquid crystals form an angle with the boundary surface (Fig. 88). For this reason, the local properties are not axially symmetric with respect to an axis normal to the interface. C-type smectics have properties typical of biaxial crystals. If long molecules forming a C-type smectic are optically active, and if the number of left- and right-hand types of molecules is not the same, the structure of the smectic becomes very complicated. In this case, in

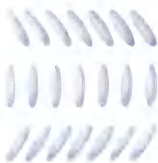


Fig. 89. Precession of the molecular axes of a C-type smectic with optically active molecules during a layer-to-layer transition



Fig. 90. Orientation order of molecules in a nematic

! Liquid crystals have many optical, electrical, magnetic, and other properties typical of crystals, but at the same time retain many mechanical properties typical of liquids (for example, fluidity).

■ layer-to-layer transition the direction of inclination precesses about the normal to the interface between the layers (Fig. 89).

In addition to A-, B-, and C-type smectics, there are some other types (H, D, E, ...) which will not be considered in this book.

NEMATICS. These liquid crystals do not have a spatial ordering. Anisotropy in their properties appears as a result of orientational ordering in their long molecules (Fig. 90), and the long-range order in the arrangement of the centres of mass of their molecules is not observed, as is typical of the binary distribution function for liquids. The line of orientation of nematic molecules serves as a preferred direction. This line is the symmetry axis for the properties of the nematic, the two directions along this line being equivalent. If the molecules possess a dipole moment, the orientation of dipoles in these two directions is equally probable: the dipole moments of one half of molecules are oriented in one direction, and of the other half, in the opposite direction. For this reason, a nematic is optically a uniaxial crystal, its optical axis coinciding with a preferred direction. Nematics can be found only among the materials in which the right- and left-handed forms of molecules coincide. If they are different, their amounts are equal (racemic system).

CHOLESTERIC. If an excess of right- or left-handed molecules is created in a nematic, the structure of the nematic phase is distorted (namely, spiral-type distortion appears in the structure). This type of distortion is observed, in particular, for a pure ester of cholesterol. For this reason, a spiral phase appearing here is called cholesteric. In this case, just as for the nematic phase, the distribution of centres of mass of the molecules does not exhibit a long-range order, and the local properties in each region are characterized by the direction of orientation of molecules in it. However, in contrast to nematics, the direction of preferential orientation changes upon transitions from one region to another, as a result of which a helical structure appears (Fig. 91). The spirals can have right-handed as well as left-handed rotation depending on the type of molecules in excess. Obviously, cholesterics can be found only among substances whose right- and left-handed forms of molecules are different and present in different amounts (nonracemic systems).

PROPERTIES AND APPLICATIONS OF LIQUID CRYSTALS. Liquid crystals have very important optical properties which have found a wide application and aroused

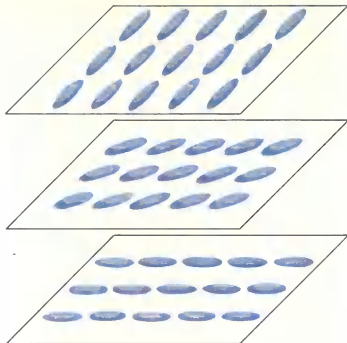


Fig. 91. To the explanation of a cholesteric structure

an interest toward their investigation. Nematics, as well as A-type smectics, are uniaxial crystals whose properties readily change under external effects over a wide range. This opens wide opportunities for controlling light flows with the help of liquid crystals.

Owing to helical periodicity in their structure, cholesterics exhibit diffractive properties in the visible part of the spectrum. Since the pitch of a helix changes under the action of external factors, say, temperature, these external effects can also be used to control the light flow.

Electric and magnetic fields produce a strong effect on the properties of liquid crystals. At the present time, the investigation of these effects has become a subject of intense scientific research, and the results obtained are used in practice. Digital indicators (displays) based on liquid crystals are well known. A method has been developed for obtaining visual images in microwave radiation. The advantages of liquid-crystal films are their comparatively low cost and low electric power consumptions.

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1. What is the physical interpretation of the pair distribution function?
2. In which phenomena and how are structural properties of liquids manifested?
3. What basic mechanisms of emergence of anisotropy exist in liquid crystals?

Sec. 37. LIQUID SOLUTIONS

The physical aspect of dissolution and its basic quantitative characteristics are considered. The dependence of solubility on temperature and pressure is analyzed. State diagrams of solutions are given.

DEFINITION. Liquid solutions are mixtures of two or several substances in the liquid state. If the amount of one of the substances in a solution is considerably larger than the others, it is called the solvent, other substances are called solutes. Solutions containing two substances are called binary.

QUANTITATIVE CHARACTERISTICS. It is convenient to characterize the relative concentration of substances in a solution by its molar concentration which is defined as the ratio of the number of moles of a substance in the solution to the total number of moles:

$$q_1 = v_1 / (v_1 + v_2), \quad q_2 = v_2 / (v_1 + v_2), \quad q_1 + q_2 = 1. \quad (37.1a)$$

This characteristic is convenient since it corresponds to the fraction of the number of molecules (or atoms) of each of the substances in the total number of molecules in a solution. Indeed, by the definition of the number of atoms, we have $N_1 = N_A v_1$ and $N_2 = N_A v_2$, where N_A is the Avogadro number. Hence, we can rewrite Eq. (37.1a) in the form

$$q_1 = N_1 / (N_1 + N_2), \quad q_2 = N_2 / (N_1 + N_2), \quad q_1 + q_2 = 1. \quad (37.1b)$$

The concentration is frequently characterized by the relative values of the masses of components of a solution. In this case, the following formulas are used instead of (37.1) for the concentrations q'_1 and q'_2 :

$$q'_1 = m_1 / (m_1 + m_2), \quad q'_2 = m_2 / (m_1 + m_2), \quad q'_1 + q'_2 = 1, \quad (37.2)$$

where m_1 and m_2 are the masses of the components in the solution.

SOLUBILITY. A solution can be formed either by dissolving a solid or a gas in a liquid, or by mixing liquids. Different situations are possible in this case.

Any number of components can be present in a solution. In some cases, there is a limit on the concentration of one of the substances. If the amount of this substance is in excess of the solubility limit, it will not dissolve. For example, we cannot dissolve an inordinately large amount of sugar in a given amount of water. In this case, the maximum equilibrium concentration is called solubility. It depends on temperature and pressure. Solid substances always have a concentration limit when they are dissolved in liquids. On the other hand, liquids can usually be mixed in any proportions (for example, alcohol and water).

HEAT OF SOLUTION. The mechanism of solution consists in rupture of the bonds between molecules of each of the initial substances and in the formation of new bonds between molecules of substances in a solution. In many cases, molecules of a substance dissociate into their components, viz. ions (in salts, alkali, etc.) during solution.

Usually, a certain amount of energy is spent for dissociation of molecules during dissolution. Consequently, the substances are cooled upon solution. The energy spent for solution is called the heat of solution.

After dissociation of molecules of the substance being dissolved, the forces of attraction between the solute and the solvent molecules may become so large that molecular complexes are formed. In this case, the internal energy increases at the expense of the work done by the attractive forces, and heating takes place. If this heating exceeds cooling accompanying the dissociation of molecules, the net result of the solution process is heating. The amount of heat liberated in this case is also called the heat of solution. An example of such a process is the solution of acids in water. The interaction between molecules in gases is very weak. Therefore, solution of gases is accompanied by a liberation of heat in most cases.

IDEAL SOLUTIONS. These are solutions for which the heat of solution is equal to zero. Obviously, the nature of interaction between the solute molecules and the solvent molecules in these solutions is the same as for the solvent molecules. This means that the interaction between molecules in the solution does not change if we substitute a certain number of solvent molecules for the same number of solute molecules and vice versa.

RAOULT'S LAW. From the condition of dynamic equilibrium at the interface between a saturated vapour and a solution it follows that the saturated vapour pressure above the solvent must be less than that above the pure solvent by as many times as the density of solvent molecules in the solution is less than that of the pure solvent, i.e. when it does not contain any solute molecules. In other words, the saturated vapour pressure decreases in direct proportion to the concentration of the solvent in a solution:

$$p_1 = v_1 p_1^{(0)} / (v_1 + v_2), \quad (37.3)$$

! With increasing temperature, the solubility of substances with positive heat of solution decreases, while with negative heat of solution, it increases.

where p_1 is the saturated vapour pressure above the solution and $p_1^{(0)}$ is the saturated vapour pressure above the pure

solvent. Similarly, for the saturated vapour pressure p_2 of the solute we obtain

$$p_2 = v_2 p_2^{(0)} / (v_1 + v_2). \quad (37.4)$$

Formulas (37.3) and (37.4) express the Raoult law for ideal solutions. However, this law is satisfied sufficiently well for all weak solutions also (not necessarily ideal), if we consider the saturated vapour of the solvent. This is due to the insignificant concentration of the solute, which cannot noticeably change the interaction between solvent molecules as a whole.

The saturated vapour pressure of nonideal solutions changes not only due to a change in the density of molecules near the surface, but also due to a change in the forces of interaction between the solvent and solute molecules in the solution. This may cause a deviation from the values predicted by the Raoult law to either side. There is no law as simple as Raoult's law for nonideal solutions.

HENRY'S LAW. The expression (37.4) for the Raoult law can be read from right to left. In this case, it will characterize the concentration of a substance in a solution if the saturated vapour pressure p_2 above it is maintained at a constant value:

$$q_2 = \alpha p_2, \quad (37.5)$$

where $\alpha = 1/p_2^{(0)}$.

The concentration of a gas dissolved in a liquid is proportional to the pressure of the gas above the surface of the liquid. For this reason, in particular, carbon dioxide is supplied under a high pressure for obtaining soda water.

TEMPERATURE DEPENDENCE OF SOLUBILITY. This dependence can be predicted on the basis of the Le Chatelier-Brown principle (see Sec. 23). It is determined by the sign of the heat of solution.

If the solution of a substance is accompanied by heating, an attempt to heat it further by adding the solute after saturation results in its precipitation (the solution is already saturated!). Hence it follows from the Le Chatelier principle that the solubility of substances with a positive heat of solution decreases with increasing temperature.

On the other hand, if a substance is cooled upon solution, an attempt to cool it further by adding the solute after saturation also leads to its precipitation. Consequently, the solubility of substances with a negative heat of solution decreases or increases with temperature. In particular, it was mentioned above that for most gases the heat of solution is

$$p_i = p_i^0 v_i / (v_1 + v_2)$$

?

1. Which factors make the heat of solution positive or negative?
2. Why do Raoult's and Henry's laws hold only for ideal solutions?

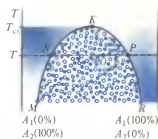


Fig. 92. Constitution diagram of a binary mixture with the upper critical temperature of mixing

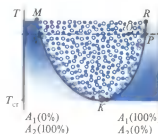


Fig. 93. Constitution diagram of a binary mixture with the lower critical temperature of mixing

negative. This means that the solubility of gases increases with temperature in most cases.

BINARY CONSTITUTION DIAGRAMS FOR SOLUTIONS. The behaviour of a solution is usually investigated under atmospheric pressure. In this case, the independent parameters are the relative concentrations of the components, and the temperature. Hence, the state of a binary mixture can be characterized by a point on the plane in the Cartesian coordinate system with the concentration of the components along the X -axis and the temperature along the Y -axis.

Figure 92 shows the constitution diagram for liquids A_1 and A_2 which are mixed in arbitrary amounts only at a sufficiently high temperature. At a lower temperature, these liquids cannot be mixed in arbitrary proportions. The line MNK characterizes the saturated solution of liquid A_1 in liquid A_2 , while the points to the left of this line correspond to unsaturated solution of A_1 in A_2 . The line RPK describes the saturated solution of liquid A_2 in liquid A_1 , while the points to the right of this line correspond to unsaturated solution of A_2 in A_1 . The region below the curve $MNKPR$ describes the state of the binary system comprising the saturated solution of A_1 in A_2 and the saturated solution of A_2 in A_1 . These saturated solutions have different densities, owing to which the heavier component occupies the lower part of the vessel. The components are divided by the interface which allows us to speak about the binary system. Above the critical temperature T_{cr} , liquids A_1 and A_2 mix in any proportions.

The states of a binary system can be characterized by a lever rule which is similar to that described in Sec. 30. For example, in the states characterized by the point O (Fig. 92), the masses m_{12} and m_{21} of saturated solutions are inversely proportional to the lengths of the segments OP and ON :

$$m_{12}/m_{21} = |OP|/|ON|. \quad (37.6)$$

We recommend that the reader derive this rule independently as an exercise.

Figure 93 shows the constitution diagram of liquids A_1 and A_2 which are mixed in arbitrary amounts only at a sufficiently low temperature. At a higher temperature, these liquids cannot be mixed in arbitrary proportions. This case is similar to the previous one, the only difference being that the unlimited mixing region now lies below the temperature T_{cr} which is called the lower critical temperature of mixing.

Finally, the situation is possible when there are two critical temperatures of mixing—the upper and the lower one.

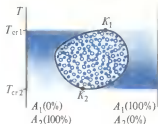


Fig. 94. Constitution diagram of a binary mixture with two critical temperatures of mixing

A typical constitution diagram for this case is shown in Fig. 94. The region inside the closed curve corresponds to the state of the binary system. Different regions in this diagram have the same sense as the corresponding regions in Figs. 92 and 93.

However, under real conditions at atmospheric pressure the critical temperature can be attained only rarely (the upper one because the solution boils at a lower temperature and the lower one because it freezes at a higher temperature).

Example 37.1. The number v' of moles of dissolved sugar constitutes 3% of the number v of moles of water. The saturated vapour pressure for water at the temperature under consideration is $p_0 = 2.66$ kPa. Find the pressure of water vapour above the sugar solution.

In accordance with the Raoult law, we can write

$$p = p_0 (1 - v'/v) = 2.58 \text{ kPa.}$$

Sec. 38. BOILING OF LIQUID SOLUTIONS

The peculiarities of boiling and constitution diagrams of binary mixtures are considered. The possibilities of separating the components and elevating the boiling point are discussed.

PECULIARITIES OF BOILING OF SOLUTIONS. The saturated vapour pressure of components above a solution depends on their concentration and is generally not the same. For a given pressure, the saturated vapour pressure of one of the components above a certain temperature may become equal to the external pressure which, however, is not equal to the saturated vapour pressure for the other component at this temperature. For these parameters, boiling is attained for the first component and not for the second. Hence, the first component will start vaporizing vigorously, while the second will be converted into vapour by evaporation, i.e. not so vigorously. As a result, the concentration of components in the vapour differs from their concentration in the boiling liquid. This leads to a change in the relative concentration of the boiling component of the liquid, and hence in its boiling temperature. Thus, vaporization of a solution is a more complicated process than vaporization of a pure liquid.

BINARY CONSTITUTION DIAGRAMS. Constitution diagrams give the most visual representation of the state of a vapour-liquid solution system. Usually, we are interested in the behaviour of the system at a constant (atmospheric) pressure. In this case, the state of the system is characterized by two independent parameters, viz. the composition and temperature. Consequently, a state of the system can be characterized by a point on the plane formed by plotting the

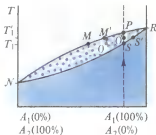


Fig. 95. The most common diagram of boiling for two unlimitedly mixing liquids

component concentrations along the X -axis and temperature along the Y -axis.

Figure 95 shows the simplest constitution diagram of a binary mixture whose components can be mixed in any proportions. The region bounded by the closed curve $NMPRSN$ corresponds to two-phase states, when a saturated vapour and a solution exist simultaneously in the volume. A one-phase state, i.e. only the solution, exists below NSR . The region above $NMPR$ corresponds to one-phase states in the form of vapour.

At temperature T_1 the state described by the point S corresponds to a pure solution, whose concentration is determined by the abscissa of this point, while the point M characterizes the vapour state at the same temperature T_1 , the concentration of the components being determined by the abscissa of the point M . The point O corresponds to a two-phase system. The total concentration of the components in the system (the sum of the concentrations of the liquid and gaseous phases) is given by the abscissa of this point, and the ratio of the masses of the liquid and the gaseous phase is inversely proportional to the ratio of lengths of segments $|OS|$ and $|OM|$ (lever rule).

Suppose that a closed vessel contains a solution whose concentration is given by the abscissa of the point S at a temperature below T_1 . As the temperature increases, the system remains in the one-phase state until the temperature T_1 is attained, corresponding to a state in which boiling of the solution begins (point S). The concentration of the vapour being formed is described by the point M . Consequently, the composition of the solution changes as a result of boiling. It can be easily seen that the concentration of the component A_1 in the solution increases. This leads to an elevation of the boiling point of the solution. If boiling occurs in a closed vessel whose volume changes in the process of boiling in such a way that the pressure is maintained at a constant value (with the help of a moving piston), the ratio of the total concentrations of the components of the two phases remains the same during boiling. Hence, the change in the state of the system during boiling is described by the motion of the point along SP . For example, at a point O' the temperature of the system is T_1' , the ratio of the total amount of A_1 and A_2 being the same as at the point S , and the ratio of the masses of the gaseous and liquid phases being equal to the ratio $O'S' : O'M'$. As point P is reached, the entire volume is filled with vapour while the ratio of the masses of components A_1 and A_2 remains the same as for liquid at the point S corresponding to the beginning of boiling. Thus, a liquid

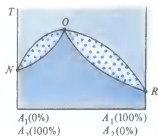


Fig. 96. Constitution diagram with a maximum for a binary mixture

solution vaporizes not at a constant temperature but in a certain temperature interval depending on the initial concentration of the solution.

SEPARATION OF SOLUTION COMPONENTS. If a system is not contained in a closed vessel and if the vapour formed during boiling is removed from the surface of the boiling solution, the concentration of the solution will change and its boiling point will rise just as in the previous case. However, in this case the system will contain only one phase all the time. Consequently, the point representing the state of the system moves along the curve $SS'R$. When the point R is attained, the component A_2 is completely boiled away, and pure liquid A_1 remains in the vessel. This phenomenon is used in one of the most widespread methods of separation of a liquid solution into its components. The vapour is mainly enriched in the substance A_2 but also contains a certain amount of the substance A_1 . Hence the vapour can be condensed and the process repeated. The concentration of the substance A_2 in the vapour formed in the repeated process is even higher. By repeating this process, we can separate the components A_1 and A_2 to any degree of purity.

Along with the most common phase diagram considered above, there are also other types of diagrams. One such diagram is shown in Fig. 96. The two-phase region is bounded by a loop-shaped curve. The point O corresponds to a state for which the liquid and the saturated vapour have the same composition. Moreover, if boiling occurs in an open vessel, the point O represents a state to which the boiling solution comes regardless of whether its initial concentration was characterized by a point on the right or left of the abscissa of the point O . After attaining the concentration corresponding to the point O , the solution boils as a pure liquid at a constant temperature, since its concentration does not change as a result of boiling. There are also other phase diagrams which will not be considered in this book.

ELEVATION OF THE BOILING POINT OF A SOLUTION. The boiling point of a saturated solution of a nonvolatile substance is higher than the boiling point of the pure solvent. In order to verify this, we take into consideration the fact that the saturated vapour pressure above a solution is lower than above the pure solvent. This means that on the liquid-vapour phase diagram (see Fig. 92), the solution-vapour curve lies below and to the right of the curve AK corresponding to the pure liquid-vapour system, which indicates that at a fixed pressure, the boiling point of the solution of a nonvolatile substance is higher than for pure solvent.

Sec. 39. OSMOTIC PRESSURE

The mechanism of emergence, regularities, and different manifestations of osmotic pressure are considered.

MECHANISM OF EMERGENCE. Suppose that the solution of a substance and the pure solvent are separated by a semipermeable membrane which lets through the molecules of the solvent and is impermeable for the molecules of the solute (Fig. 97). Such membranes are usually films of plant or animal origin. After a sufficiently long interval of time, equilibrium sets in and the molecules of the solvent freely interact with one another through the semipermeable membrane. The nature of this interaction is not completely clear so far. The semipermeable membrane cannot be treated purely mechanically by assuming that it has pores permeable for one type of molecules and impermeable for the other from purely geometrical point of view. Actually, we apparently have a more complicated interaction between the molecules and the semipermeable membrane, involving the penetration of the solvent into the material of the membrane. But regardless of the details of this mechanism, the pressure on the plug due to the impacts of the solvent molecules on both sides must be the same in the equilibrium state. On the other hand, the pressure of the solute is not transmitted through the membrane to the solvent on the other side. Thus, the total pressure on one side of the membrane, equal to the sum of the pressures of the solvent and the solute, is higher than the pressure on the other side of the membrane, equal to the pressure of the solvent. As a result, the level of the pure solvent becomes lower than the level of the solution (Fig. 97). If initially the level of the pure solvent was the same as the level of the solution, the pure solvent will penetrate through the semipermeable membrane to the region occupied by the solution, which leads to an increase in pressure and the level of the solution in this region. The process of penetration of a solvent through a semipermeable membrane is called **osmosis**. The pressure difference created between the regions occupied by the pure solvent and the solution separated by a semipermeable membrane is called **osmotic pressure**.

FACTORS DETERMINING THE OSMOTIC PRESSURE. The molecules of a solute in a sufficiently diluted solution behave as molecules in a rarefied gas, since in accordance with the law of equipartition of energy, their kinetic energy depends only on temperature. The osmotic pressure is equal to the pressure of the rarefied gas of these molecules, i.e. it can be calculated with the help of the formula for ideal gases:

$$\Pi = nkT/V = \nu RT/V, \quad n = \nu N_A, \quad kN_A = R, \quad (39.1)$$



Fig. 97. To the explanation of the osmotic pressure

where n is the total number of solute molecules in the volume V and ν is the number of moles of the molecules. Formula (39.1) is the analytic expression of the **Van't Hoff law**. The osmotic pressure of weak solutions is independent of the nature of the solvent and the solute and depends only on the molar concentration of the solute. In order to estimate the order of magnitude of the osmotic pressure, it is useful to note that in the presence of a mole of molecules in one litre volume, the osmotic pressure is equal to 2.39 MPa. However, the walls of the vessel do not experience this pressure, since it also acts on the free surface of the liquid, and the stresses appearing in the surface layer of the liquid compensate the osmotic pressure. Only hydrostatic pressure acts on the vessel walls.

MANIFESTATION OF OSMOTIC PRESSURE. Osmotic pressure can be effectively demonstrated in a lecture room. For example, if we drop a potassium ferrocyanide crystal into a 5% solution of blue vitriol, it is covered by a semipermeable envelope whose dimensions are increased by the osmotic pressure acting from the inside. A kind of an "artificial cell" is created, which grows and forms a dendrite structure.

If we fill an animal bladder with alcohol, tie it and immerse into water, the latter penetrates into the bladder. It blows up and may burst. Osmosis plays an extremely important role in the world of animals and plants. Most of the partitions in the living organisms and plants are semipermeable. For example, the osmotic pressure in plant cells reaches several atmospheres, owing to which ground water can rise along the trunk of a tree to a large height. Osmotic pressure facilitates the transition of water from some liquid media to the others through semipermeable membranes in living organisms.

Example 39.1. Find the osmotic pressure when 50 g of methyl alcohol CH_3OH ($M_r = 32$) are dissolved in 10 l of water. The temperature of the solution is 27°C .

The concentration of the solute is low, so we can use formula (39.1) for calculating the pressure:

$$\Pi = \frac{m}{M} \frac{RT}{V} = \frac{50 \times 10^{-3}}{32} \frac{8.31 \times 300 \times 10^3}{10 \times 10^{-3}} \text{ Pa} = 389.5 \text{ kPa}.$$

Sec. 40. CHEMICAL POTENTIAL AND PHASE EQUILIBRIUM

Systems with varying number of particles are considered and the chemical potential is defined. The concept of chemical potential is used for analyzing the conditions of phase equilibrium.

CHEMICAL POTENTIAL. There are systems that consist not just of two components or two phases, but involve a large number of components. Their composition varies depending on temperature, pressure, etc. If there are several components in a system, its internal energy depends on the number density n_i of each component. It is convenient to take volume V and entropy S as other independent variables determining the internal energy:

$$U = U(S, V, n_1, n_2, \dots, n_i). \quad (40.1)$$

Then

$$dU = \left(\frac{\partial U}{\partial S} \right)_{V, n_i} dS + \left(\frac{\partial U}{\partial V} \right)_{S, n_i} dV + \sum_i \left(\frac{\partial U}{\partial n_i} \right)_{V, S, n_j} dn_i, \quad (40.2)$$

where the summation is carried out over all n_i 's, and when we take a partial derivative with respect to n_i , the remaining $n_j \neq n_i$ are assumed to be fixed. Formula (40.2) is a generalization of Eq. (23.14) for a multicomponent system. These formulas coincide for $dn_i = 0$, i.e. for a one-component system. Comparing these formulas, we get

$$T = \left(\frac{\partial U}{\partial S} \right)_{V, n_i}, \quad -p = \left(\frac{\partial U}{\partial V} \right)_{S, n_i}. \quad (40.3)$$

Equation (40.2) then assumes the form

$$dU = T dS - p dV + \sum_i \mu_i dn_i, \quad (40.4)$$

where

$$\mu_i = \left(\frac{\partial U}{\partial n_i} \right)_{V, S, n_j}, \quad n_j \neq n_i. \quad (40.5)$$

Similarly, we can modify the remaining thermodynamic functions considered in Sec. 23 if we take into account the varying number of particles. For example, the Gibbs function G defined by (23.13) can be assumed to depend on pressure p , temperature T , and concentration n_i of various components of the system:

$$G = G(T, p, n_1, n_2, \dots, n_i). \quad (40.6)$$

If we take (23.18) into account, the relation

$$dG = \left(\frac{\partial G}{\partial T} \right)_{p, n_i} dT + \left(\frac{\partial G}{\partial p} \right)_{T, n_i} dp + \sum_i \left(\frac{\partial G}{\partial n_i} \right)_{T, p, n_j} dn_i \quad (40.7)$$

becomes

$$dG = -S dT + V dp + \sum_i \left(\frac{\partial G}{\partial n_i} \right)_{T, p, n_j} dn_i. \quad (40.8)$$

Combining (23.12) and (23.13), we get

$$dG = dU + p dV + V dp - T dS - S dT. \quad (40.9)$$

Taking into account (40.8) and (40.4), we obtain

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, p, n_j}, \quad n_j \neq n_i. \quad (40.10)$$

Hence, formula (40.8) finally becomes

$$dG = -S dT + V dp + \sum_i \mu_i dn_i. \quad (40.11)$$

In a similar way, we obtain the following expressions for enthalpy and free energy instead of (23.15) and (23.16):

$$dH = T dS + V dp + \sum_i \mu_i dn_i, \quad (40.12)$$

$$dF = -S dT - p dV + \sum_i \mu_i dn_i. \quad (40.13)$$

Here

$$\mu_i = \left(\frac{\partial H}{\partial n_i} \right)_{S, p, n_j}, \quad \mu_i = \left(\frac{\partial F}{\partial n_i} \right)_{T, V, n_j}, \quad n_j \neq n_i. \quad (40.14)$$

The quantity μ_i is called the **chemical potential**. Formulas (40.14), (40.10), and (40.5) define it for different variables taken as independent.

EQUILIBRIUM CONDITIONS. It follows from formula (23.17) that at constant pressure and temperature, the equilibrium condition is expressed as follows:

$$(dG)_{T, p} = 0. \quad (40.15)$$

A system may consist of many components, but in all practically important cases the number of phases is equal to two or three. For the sake of definiteness, we shall assume that there are two phases l and 2 and two components a and b . The Gibbs function for the entire system is equal to the sum of the Gibbs functions of its phases. As usual, we shall assume that the phases are homogeneous. It follows from the conservation condition for the total number of particles in the entire system that

$$n_{a1} + n_{a2} = \text{const}, \quad n_{b1} + n_{b2} = \text{const}, \quad (40.16)$$

whence

$$dn_{a1} + dn_{a2} = 0, \quad dn_{b1} + dn_{b2} = 0. \quad (40.17)$$

The Gibbs functions of the first and second phases can be expressed as follows:

$$dG_1 = -S dT + V dp + \mu_{a1} dn_{a1} + \mu_{b1} dn_{b1}, \quad (40.18)$$

$$dG_2 = -S dT + V dp + \mu_{a2} dn_{a2} + \mu_{b2} dn_{b2}.$$

For constant T and p , the following condition must be satisfied in equilibrium:

$$(dG)_{T,p} = (dG_1)_{T,p} + (dG_2)_{T,p} = 0, \quad (40.19)$$

which in combination with (40.18) and (40.17) leads to the following equation:

$$(\mu_{a1} - \mu_{a2}) dn_{a1} + (\mu_{b1} - \mu_{b2}) dn_{b1} = 0. \quad (40.20)$$

Since n_a and n_b are independent, it follows that

$$\mu_{a1} = \mu_{a2}, \quad \mu_{b1} = \mu_{b2}. \quad (40.21)$$

Similar calculations made for a larger number of components lead to the same kind of expressions for the chemical potential of each component for all phases. Let μ_{ij} be the chemical potential of the i th component in the j th phase. Under equilibrium conditions at constant temperature and pressure, we have

$$\mu_{i1} = \mu_{i2} = \dots = \mu_{ij}, \quad i = 1, 2, \dots, \quad (40.22)$$

i.e. the chemical potential for each component has the same value in all the phases under equilibrium conditions at constant pressure and temperature.

CHEMICAL POTENTIAL FOR A ONE-COMPONENT SYSTEM. Obviously, the above statement is valid for a one-component system as well. In this case, for a pure phase Eq. (40.11) yields

$$(dG)_{T,p} = \mu dn, \quad (40.23)$$

Consequently, the Gibbs function can increase only due to an increase in the mass of the phase. On the other hand, it is clear that the Gibbs function is proportional to the total number of molecules in the system. Hence, on the basis of (40.23), we can write

$$\mu = G/n, \quad (40.24)$$

i.e. the chemical potential of a one-component system is equal to the mean value of the Gibbs function per molecule.

Sec. 41. PHASE RULE

Phase rule is derived and used to analyze possible types of phase diagrams.

FORMULATION OF THE PROBLEM. How many independent parameters characterize the state of K -component system comprising Φ phases?

The answer to this question is given by the phase rule derived by Gibbs.

PHASE RULE. The equilibrium condition for each of the system at constant temperature and pressure can be written, in accordance with (40.11), as follows:

$$(dG)_{T,p} = \sum_{ij} \mu_{ij} dn_{ij} = 0, \quad (41.1)$$

where μ_{ij} have the same sense as in (40.22), and dn_{ij} is the differential of the i th component in the j th phase. These equations involve $K\Phi$ quantities μ_{ij} , not all of which are independent. Firstly, the law of constant proportions for each phase yields one relation connecting chemical potentials (hence there are Φ such relations in all). Secondly, in accordance with (40.22), the chemical potentials of each component in all phases must be the same:

$$\mu_{i1} = \mu_{i2} = \dots = \mu_{i\Phi}. \quad (41.2)$$

For each i we have $\Phi - 1$ equalities, and for K components we get $K(\Phi - 1)$ conditions. Consequently,

the total number of independent variables μ_{ij} is

$$K\Phi - \Phi - K(\Phi - 1) = K - \Phi. \quad (41.3)$$

In addition, the temperature and pressure are also two independent parameters. Therefore, the total number of independent parameters characterizing the equilibrium state of the system consisting of K components and comprising Φ phases is equal to

$$C = K - \Phi + 2. \quad (41.4)$$

Equation (41.4) expresses the **Gibbs phase rule**. It gives the number of degrees of freedom of a system, which cannot be negative, i.e. $C \geq 0$. This means that

$$\Phi \leq K + 2, \quad (41.5)$$

i.e. the number of phases which can be in equilibrium cannot exceed the number of components by more than two. This statement is another possible formulation of the phase rule (41.4).

PHASE DIAGRAMS. The state of each phase is determined by the pressure, temperature, and $K-1$ values of the chemical potentials of the components, since K chemical potentials are connected through one relation expressing the constancy of the number of moles in the system. Hence, such a state of the system is characterized by a point in a $K-1+2=(K+1)$ -dimensional space. For a one-component system, a state is represented by a point on the plane as was done, for example, while considering the processes in an ideal gas (see Sec. 18). On the other hand, for a multiphase system in equilibrium, the number of degrees of freedom is determined by the phase rule (41.4). Suppose, for example, that we have a two-phase one-component liquid-vapour system (see Sec. 32). In this case, $\Phi=2$, $K=1$, and hence

$$C=1. \quad (41.6)$$

This means that the state of the two-phase system is represented by the line AK on the phase diagram (see Fig. 70) which depicts the states of the one-component system as points on the two-dimensional plane $[T, p]$.

In the case of a one-component system, the number of degrees of freedom of a three-phase state ($\Phi=3$) is

$$C=0. \quad (41.7)$$

This means that three phases (gas, liquid, and solid) can be in equilibrium only for a unique relation connecting the parameters which characterize this system. The equilibrium state for the three phases is depicted by a point called the triple point. This question will be considered in greater detail in the next chapter.

When analyzing the boiling of liquid solutions (see Sec. 38), we assumed that the system consisted of two components ($K = 2$). Consequently, we should have used a three-dimensional space in order to represent the states of each of its phases. However, we fixed one of the parameters (pressure) and characterized the state of the system by two parameters, viz. temperature and concentration. The number of degrees of freedom of the two-phase state in this case is equal to

$$C = 2 - 2 + 2 = 2. \quad (41.8)$$

For this reason, the two-phase states shown in Figs. 95 and 96 occupy a certain area separated by phase curves from the one-phase states.

PROBLEMS

- 4.1. Calculate the osmotic pressure for 10 g of ethyl alcohol ($M_r = 46$) dissolved in 10 l of water at 20°C.
- 4.2. Find the mass m of sugar ($M_r = 342.3$) dissolved in 200 g of water at 25°C, if the osmotic pressure is 0.196 MPa.
- 4.3. Find the change in the melting point of ice if the pressure has changed from 0.098 to 0.196 MPa. The density of ice $\rho = 0.9$ g/cm³ and its heat of fusion is 334 kJ/kg.
- 4.4. Calculate the heat of evaporation of water and its saturated vapour pressure at 50°C.
- 4.5. Find the boiling point of water under the air pressure of 0.1 and 0.1024 MPa.
- 4.6. The spherical water film, whose values of σ and L are given in Example 34.1, expands isothermally at $T = 293$ K from $r_1 = 2$ cm to $r_2 = 3$ cm. Find the change in the entropy of the film.
- 4.7. Find the inversion temperature of the differential Joule-Thomson effect and the change in temperature in the Joule-Thomson process when the pressure changes by 10.13 kPa at $t = 27^\circ\text{C}$, assuming that the Van der Waals constants for air are $a = 0.142$ Pa·m⁶/mole² and $b = 3.9 \times 10^{-7}$ m³/mole.
- 4.8. The surface tension of soap solution is 4×10^{-2} N/m. Find the additional pressure inside a soap bubble of radius 2×10^{-3} m.

- 4.9. There are 0.04 mole of sugar molecules per mole of water molecules in a solution of sugar in water. The saturated vapour pressure for water at a given temperature is 1995 Pa. Find the pressure of water vapour above the surface of the solution.
- 4.10. The Van der Waals constants for carbon dioxide are $a = 3.64 \times 10^5 \text{ Pa} \cdot \text{m}^6/\text{kmole}^2$ and $b = 4.26 \times 10^{-2} \text{ m}^3/\text{kmole}$. Find the pressure of carbon dioxide if 1 kmole occupies a volume of 1 m^3 at 100°C (use the formula for an ideal gas and the Van der Waals equation).
- 4.11. Find the temperature drop in 10 kg of nitrogen upon its expansion from 1 to 2 m^3 , assuming that for nitrogen the Van der Waals constant $a = 1.36 \times 10^5 \text{ Pa} \cdot \text{m}^6/\text{kmole}^2$.
- 4.12. The saturated vapour pressure of ethyl alcohol $\text{C}_2\text{H}_5\text{OH}$ at 40°C is 17.69 kPa, while at 68°C it is 67.7 kPa. Find the change in entropy upon evaporation of 5 g of ethyl alcohol at 50°C .
- 4.13. The density of a substance at 0°C is 10 g/cm^3 , and the mean value of the volume expansion coefficient in the temperature interval from 0 to 300°C is $1.85 \times 10^{-4} \text{ K}^{-1}$. Find the density of this substance at 300°C .
- 4.14. The temperature coefficient of thermal expansion of mercury is $1.82 \times 10^{-4} \text{ K}^{-1}$. Find the compressibility of mercury, if it is known that the external pressure must be increased by 4.6 MPa upon heating by 1 K in order to maintain the volume constant.
- 4.15. The surface tension of mercury is 0.49 N/m. Find the temperature increase for a drop of mercury obtained when two drops of radius 0.5 mm each merge.
- 4.16. The additional pressure inside a soap bubble whose surface tension is $4.3 \times 10^{-2} \text{ N/m}$ is equal to 266 Pa. Find the radius of the bubble.
- 4.17. Alcohol flows out of a vessel through a vertical capillary of inner radius 1 mm. The drops fall every second. What time does it take for 20 g of alcohol to flow out?
- 4.18. The inner radius of an open capillary immersed into a vessel with mercury is 1 mm. The level of mercury in the capillary is lower than the level of mercury in the vessel by 3 mm. Find the radius of curvature of the mercury meniscus in the capillary.
- 4.19. Two g of common salt are dissolved in 1 l of water at $T = 300 \text{ K}$. The degree of dissociation of the common salt molecules upon dissolution is 40%. Find the osmotic pressure of the solution.
- 4.20. Find the pressure of water at a depth h if the density of water at the surface is ρ_0 and pressure is p_0 (a) when compressibility is not taken into account and (b) when the compressibility κ is taken into account. The temperature and the acceleration due to gravity are assumed to be constant.
- 4.21. Find the change in the saturated vapour pressure at the surface of a spherical water drop of radius 10^{-6} cm at 20°C , if the pressure for a flat surface is $p_0 = 2333 \text{ Pa}$. Assume that $\sigma = 0.075 \text{ N/m}$ and $\rho = 10^3 \text{ kg/m}^3$.

ANSWERS

4.1. $\Pi = 0.338 \text{ MPa}$. 4.2. $m = 10 \text{ g}$. 4.3. $dT = -0.009 \text{ K}$. 4.4. 2.383 MJ/kg ; $0.126 \cdot 10^5 \text{ Pa}$. 4.5. 99.3°C ; 100.37°C . 4.6. $\Delta S = 840 \text{ J/K}$. 4.7. 870 K ; -0.026 K . 4.8. 0.8 Pa . 4.9. 1915 Pa . 4.10. 2.87 MPa ; 273 MPa . 4.11. $\Delta T = 1.16 \text{ K}$. 4.12. $\Delta S = 14.3 \text{ J/K}$. 4.13. 9.5 Mg/m^3 . 4.14. $3.85 \cdot 10^{-11} \text{ Pa}^{-1}$. 4.15. $\Delta T = 3.3 \cdot 10^{-4} \text{ K}$. 4.16. 0.65 mm . 4.17. 26 min . 4.18. 2.5 mm . 4.19. 0.122 MPa . 4.20. (a) $p = p_0 + \rho_0 gh$; (b) $p = p_0 - (1/\kappa) \ln(1 - \kappa \rho_0 gh)$. 4.21. 260 Pa .



Solids

Physical situation: forces of attraction between molecules dominate. A stable equilibrium is attained for a certain arrangement of molecules in the vicinity of each molecule. Since this must be observed over the entire volume, the mutual arrangement of molecules is periodically repeated, and a crystalline structure appears.

Finite number of structures: since the number of possible classes of symmetry of crystal lattices is finite, the total number of different crystalline structures is limited.

Sec. 42. SYMMETRY OF SOLIDS

Symmetry elements of a solid are described and it is shown that they can be represented by reflections in a plane. Point symmetry groups are defined.

SOLIDS. The most typical feature of solids distinguishing them from other states of aggregation is the property to retain their shape and volume. Owing to this property, solids have played a major role in the formation of our concepts about space, geometrical images and relations between them as well as in developing the theory of measuring in space.

The movement of solids formed the basis for the evolution of concepts of mechanical motion and displacement of material bodies in space.

The place occupied by a material body and its shape are abstract in our mind as separate geometrical spatial images. Owing to this, ■ comparison of shape, size, and other parameters of solids becomes meaningful.

Symmetry is a very important geometrical property of solids. For example, a stone picked up on the road differs from ■ brick in that, first of all, it has an irregular shape. The words "regular" and "irregular" are a subjective reflection of objective properties of the form of material bodies, viz. their symmetry.

We say that a right cylinder is more symmetric than a right parallelepiped, while a sphere is more symmetric than a cylinder. We also say that the shape of ■ human body is symmetric as well as that of the bodies of most animals.

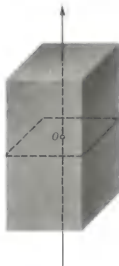


Fig. 98. Four-fold symmetry axis, symmetry plane, and centre of symmetry O

Now, we must try to give a mathematical definition of the concept of symmetry.

DEFINITION OF SYMMETRY. Symmetry is the ability of a solid to coincide with itself as a result of its movements or imaginary operations on its points. The larger the number of ways of attaining such a coincidence, the more symmetric is the shape of a body.

For example, a right circular cylinder coincides with itself upon rotation about its axis through any angle. It also coincides with itself upon a rotation through 180° about any axis perpendicular to its axis and passing through the point on the axis lying at the middle of the height. If we consider a sphere, it can be made to coincide with itself upon its rotation through any angle around an axis passing through its centre. Obviously, a sphere has much more possibilities of coincidence with itself than a cylinder. It is just this fact that is expressed in the statement that a sphere is more symmetric than a right circular cylinder.

However, symmetry consists not only in coincidences of a body with itself as a result of spatial movements. For example, there are no spatial movements that can make the left half of a human body coincide with the right half. In other words, a right-hand glove cannot be put on the left hand. By the symmetry of left and right hands we mean not the possibility of their spatial coincidence but the possibility for the right hand to coincide with the mirror reflection of the left hand.

Despite the seemingly large variety of possible symmetries of solids, they are all composed of four symmetry elements. Various combinations of these four elements make up all the possible symmetries of solids.

SYMMETRY AXIS OF THE n TH ORDER. If a body coincides with itself upon its rotation about a certain axis through the angle $2\pi/n$, this axis is called an n -fold symmetry axis. For example, a quadratic cylinder (Fig. 98) coincides with itself upon a rotation through $\pi/2$ about the axis passing through the points of intersection of the diagonals of the squares forming its bases. Consequently, this axis is a four-fold symmetry axis. Obviously, any axis of a body is a one-fold symmetry axis.

SYMMETRY PLANE. If a body coincides with itself as a result of the mirror reflection of its points in a certain plane, this plane is called the *symmetry plane of the body*. The shaded surface in Fig. 98 is a symmetry plane.

CENTRE OF SYMMETRY. If a body coincides with itself upon inversion through a certain point, this point is called the *centre of symmetry* (point O' in Fig. 98).

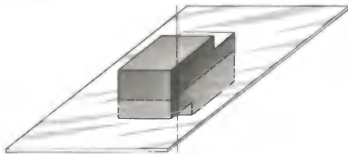


Fig. 99. A rotoreflection two-fold axis

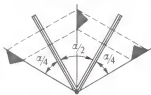


Fig. 100. A rotation as a result of two consecutive reflections in planes

THE n -FOLD ROTOREFLECTION AXIS. If a body coincides with itself upon a rotation through an angle $2\pi/n$ and reflection in a plane perpendicular to the axis of rotation, this axis is called an n -fold reflection-rotation axis. A two-fold axis of this type is shown in Fig. 99.

POINT SYMMETRY GROUPS. The totality of symmetry elements of a body is called its symmetry group. The symmetry elements considered above have a common property: they leave at least one point of a body at rest. The symmetry groups corresponding to these elements are called point groups.

All the symmetries listed above can be described by using only reflections in a plane. The rotation through an angle α can be represented by two consecutive reflections in planes intersecting along the axis of rotation at the angle $\alpha/2$ (Fig. 100). The inversion about the centre of symmetry can be reduced to three reflections in three mutually perpendicular planes, passing through the centre of symmetry.

MIRROR ISOMERS. Two bodies can be similar and made to coincide with the help of reflection in a plane, but cannot be made to coincide by any spatial movement. By way of an example, we can mention the palms of hands. Such bodies are called mirror isomers. There are many molecules that are known to be mirror isomers. They differ in their properties in the same sense as the right differs from the left. For example, they rotate in opposite directions the plane of optical polarization passing through them (if such a rotation takes place). Chemical reactions between like mirror isomers occur not in the same way as between unlike isomers. For example, the right isomers of two substances do not react in the same way as a right isomer and a left one.

Sec. 43. CRYSTAL LATTICE

Physical reasons behind the existence of periodic structure of solids are discussed. Translational symmetry and spatial symmetry groups are described. These groups form the basis for analyzing the main features of crystal lattice classification. The notation for atomic planes and directions is introduced.

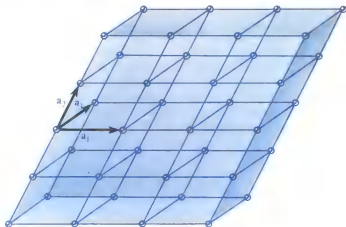
THE NECESSITY OF PERIODIC STRUCTURE. A solid is formed when the interaction between molecules (atoms or ions) is so strong that thermal motion of molecules is not so significant as in the case of liquids and especially gases. As a result, the molecules of a solid are arranged with respect to each other in certain precisely fixed positions and perform small thermal vibrations near equilibrium positions. The mutual arrangement of equilibrium positions is determined by equilibrium conditions. Naturally, if these conditions are satisfied in a certain region of space and stipulate some mutual arrangement of molecules in this region, they must be satisfied in another region, and hence must stipulate a similar arrangement of molecules there. This means that the mutual arrangement of molecules is repeated as we go over from one spatial region to another, i.e. solids have periodic structure. It is realized in the form of a crystal lattice, and solids themselves are crystals. The points of equilibrium for atoms, molecules, or ions constituting a crystal are called lattice sites.

Such a reasoning, however, raises the question as to why amorphous bodies like glasses and plastics, which have no periodic structure, exist along with crystals. As a matter of fact, these materials are not in equilibrium states. Their structure changes with time, approaching a crystalline state. For example, glass crystallizes in several hundreds of years. The process of its crystallization can be considerably accelerated at a high temperature, when it softens. Crystallization in plastics is considerably hampered since long molecules constituting them are entangled. In order to improve the quality of a plastic, special treatment is employed to make most of its molecules different (in their physical length, side chains, etc.). Thus, stability can be ensured even without a periodic structure.

PRIMITIVE LATTICE. The periodic structure of a crystal lattice means that there must exist a certain elementary group of atoms which, repeated in all directions, can cover the entire lattice in space. Generally speaking, the elementary group of atoms (we consider atoms for the sake of simplicity though it can be molecules or ions) as well as the lattice generated by its repetition are very complicated structures.

For this reason, it is expedient to divide the entire lattice into certain simpler sublattices each of which is quite simple. Obviously, a sublattice is also a lattice. The simplest lattice consists of elementary groups of atoms in the form of

Fig. 101. The basis of a primitive crystal lattice



parallelepipeds whose repetition covers the entire lattice (Fig. 101).

By choosing the origin of coordinates at a certain site of such a lattice, we can represent the radius vector of any other site in the form

$$\mathbf{r} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3, \quad (43.1)$$

where n_1 , n_2 , and n_3 are integers (including zero). The vectors $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ are called **basis vectors**, and the set of these vectors is called the **basis of the lattice**. The lengths of the vectors $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ are called the **primitive periods of the lattice**. The parallelepiped with the edges $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$, and having atoms at its corners is called the **unit cell of the crystal lattice**. When the numbers n_1 , n_2 , and n_3 in formula (43.1) assume all possible integral values from $-\infty$ to $+\infty$, the radius vector $\mathbf{r}$ runs through all sites of the crystal lattice and there are no lattice sites that are not described by formula (43.1). Such a lattice is called the **primitive**, or **Bravais lattice**, and its unit cell is termed the **primitive cell**.

Generally, a specific crystal lattice cannot be represented in the form of one Bravais lattice but is a combination of several such lattices. For this reason, it is called a **composite lattice**.

AMBIGUITY IN THE CHOICE OF A PRIMITIVE LATTICE BASIS. The choice of the basis of even a primitive lattice is not unambiguous. This can be easily seen from Fig. 102, where two possible structures of a primitive lattice with different bases for a two-dimensional case are shown by dashed lines. In the first case, the basis is formed by the

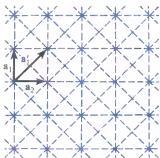


Fig. 102. Ambiguity in the choice of the basis of a crystal lattice

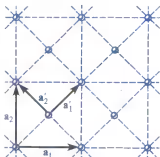


Fig. 103. Determination of the primitive lattice

vectors a_1 and a_2 , while in the second, by the vectors a'_1 and a'_2 . In the first case, the unit cell is a rectangle, while in the second it is a parallelogram. In two dimensions, each atom at the lattice site is surrounded by four unit cells. Consequently, the area occupied by an atom in the cell, equal to the total area divided by the number of atoms, is equal to the unit cell area $|a_1 \times a_2|$ in the first case and $|a'_1 \times a'_2|$ in the second.

As expected, the unit cell areas are equal in both cases, although the bases are different. These results can be easily extended to the three-dimensional case for which the choice of a unit cell in a crystal is also ambiguous, but the unit cell volume is the same for all possible ways of choosing the basis. This volume is calculated by using the formula for the volume of a parallelepiped:

$$V_0 = a_1 \cdot a_2 \times a_3. \quad (43.2)$$

This is the volume per atom in a crystal lattice.

Primitive bases differ from one another in the length of basis vectors or, which is the same, in the primitive lattice periods. A Bravais lattice with minimal primitive periods is called the reduced lattice.

It is not always easy to determine at first sight whether a given lattice is primitive or composite. This can be done best of all if we consider the entire lattice rather than its small part equal approximately to a unit cell. The problem consists in determining whether it is possible to draw three systems of perpendicular planes such that all the atoms of the lattice are at the points of intersection of the planes and there are no atoms beyond these points.

By way of an example, let us consider a plane lattice (Fig. 103). If we take the vectors a_1 and a_2 as the basis, the lattice seems to be composite since the atoms at the centres of squares do not lie at the sites of the primitive lattice constructed on this basis. It seems at a first glance that one more primitive lattice is required, and hence the initial lattice is not of the Bravais type. This, however, is wrong. Let us take the vectors a'_1 and a'_2 as the basis. In this basis, the entire initial lattice can be represented as a Bravais lattice. Hence the initial lattice is also primitive.

This becomes clear if we consider the system of dashed lines (Fig. 103).

TRANSLATIONAL SYSTEM. Owing to its infinite dimensions, the lattice has, in addition to symmetries typical of solids, a translational symmetry, i.e. the ability of self-coincidence as a result of translational motion. For example, if a primitive lattice is moved along one of the edges of its unit cell by an integral number of the primitive periods,



Fig. 104. To the determination of n possible order of rotation and roto-reflection axes in the crystal lattice

the lattice will coincide with itself. If the lattice is displaced by the vector $\mathbf{r}$ defined by (43.1), the self-coincidence will take place again. For this reason the vector $\mathbf{r}$ is called a **translational vector**. Thus we can say that the entire primitive lattice can be obtained from any site if we subject it to all possible translations parallel to the basis vectors.

SPACE GROUPS. Symmetry elements of a solid form point symmetry groups. If they are supplemented by the translational symmetry typical of infinite periodic structures, they will together form a symmetry group. Consequently, we can state that **crystal lattices are characterized by space symmetry groups**.

ELEMENTS OF LATTICE SYMMETRY. First of all, it should be noted that the symmetries of a lattice as a whole differ from the symmetries of its unit cell. This follows from the fact that the choice of a unit cell is ambiguous, and different unit cells may have different symmetries. Hence, the **lattice symmetry is just the symmetry of the lattice and not of its unit cell**.

It is clear that any primitive lattice has its centre of **symmetry** which may coincide with any site of a primitive **parallelepiped**, the mid-points of its edges, or the centres of its faces. Symmetry planes are also elements of lattice symmetry. As regards the symmetry axes and reflection-rotation axes, they can only be two-, three-, four-, or six-fold axes, the axes of other orders being impossible. This can be proved if we consider that during rotation the atoms of the lattice move in planes perpendicular to the axis of rotation.

Let us consider atoms lying in a certain plane. They form a plane crystal lattice whose sites create a system of regular identical polygons coinciding with one another upon rotation and hence densely (without intervals) covering the surface. Let us consider the point O (Fig. 104) at which the edges of adjoining regular polygons meet. If the number of points meeting at this point is equal to p , the angles between the edges are equal to $2\pi/p$. On the other hand, the angle between the sides of a regular n -sided polygon is equal to $\pi(n-2)/n$.

If a plane is filled by regular polygons without gaps, these angles are equal:

$$2\pi/p = \pi(n-2)/n. \quad (43.3)$$

Hence it follows that

$$p = 2n/(n-2), \quad (43.4)$$

where p and n are integers. The solutions of this equation are
 $n = 3, n = 4, n = 6.$ (43.5)

Thus, the surface can be covered without gaps by
 equilateral triangles ($n = 3$)

squares ($n = 4$)



and regular hexagons ($n = 6$) (honeycomb structure)



There are no other regular polygons capable of covering the plane without gaps.

They can be obviously supplemented by the axis $n = 2$ corresponding to the reflection in a plane passing through this axis, as well as by the trivial axis $n = 1$ corresponding to rotation through 2π . Thus, a crystal lattice may have only two-, three-, four-, and six-fold axes. Similarly, it can be proved that reflection-rotation axes may have only these orders.

As a result, we see that the number of elements of point symmetry groups in crystal lattices is finite, as well as the number of possible symmetries.

CRYSTAL CLASSES. Since composite crystal lattices consist of Bravais lattices it is expedient to classify crystals in accordance with the symmetry of the Bravais lattices (as mentioned above, we mean point symmetry in this case). Such a classification was made by Bravais. He showed that although the lattice symmetry does not necessarily coincide with the symmetry of any primitive cell, it is always possible to find a primitive cell having the same symmetry elements as the lattice on the whole. The smallest of the primitive cells including all the elements of lattice symmetry is called the **Bravais cell** or **parallelepiped**.

There are six types of Bravais primitive cells and hence, if we take into account the hexagonal lattice, seven types of lattices or seven kinds of crystal systems in all. If new atoms are placed at the centres of the faces or at the centre of the volume of the Bravais parallelepiped, this will not change the lattice symmetry but adds new types of lattices. Hence, there exist 14 types of Bravais lattices, distributed among seven crystal systems.

These lattices are described in detail in crystallography textbooks. Here, we shall confine ourselves to brief remarks only.

?

1. What is a primitive lattice?
2. Can a crystal lattice, generally speaking, be represented in the form of one primitive lattice?
3. What is a reduced primitive lattice?
4. Does the lattice symmetry coincide completely with the symmetry of its unit cell? How can you tell?
5. What orders of rotation axes are possible in a crystal lattice? Find the figures covering the plane without intervals to which these axes correspond.
6. How many types of crystal systems do you know? How many types of Bravais primitive parallelepipeds do you know?
7. What are the notations of the directions and planes in crystals?

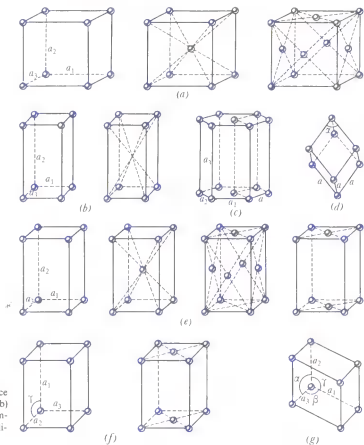


Fig. 105. Crystal classes and lattice types. Systems: (a) cubic, (b) tetragonal, (c) hexagonal, (d) rhombohedral, (e) rhombic, (f) monoclinic, and (g) triclinic

Figure 105 shows the lattices belonging to seven crystal systems. In each system (with the exception of the hexagonal system), the first picture shows the Bravais primitive cell followed by lattices obtained by centering the volume and faces of the primitive parallelepiped. This operation does not change the lattice symmetry, but the primitive cells thus obtained naturally do not coincide with the Bravais primitive cell and have symmetries differing from the lattice symmetry. As regards the hexagonal system, its unit cell has the same symmetry elements as those of the lattice, and is not a parallelepiped. The unit parallelepiped in this case is shown in the diagram along with the unit cell.

Figure 106 gives the notation for axes and angles of the Bravais primitive parallelepiped. With the help of this

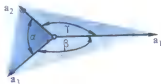


Fig. 106. Notation for axes and angles in the Bravais primitive parallelepiped

notation, the Bravais primitive cells for various crystal systems are described in Table 5.

SYMMETRIES OF COMPOSITE LATTICES. Since a composite lattice consists of primitive ones having different types of symmetry, the symmetry of a composite lattice considerably differs from the symmetry of its component primitive lattices. Besides, additional symmetry elements are possible for the composite lattice, viz. the screw axis and the mirror slip plane.

The **n -fold screw axis** is a straight line such that the motion of the lattice along this line with simultaneous rotation through $2\pi/n$ leads to its self-coincidence. Screw axes of the same order differ in the direction of rotation, i.e. can be "left-handed" and "right-handed".

The **mirror slip plane** is a plane such that reflection in it with simultaneous displacement by a certain distance parallel to this plane leads the lattice to self-coincidence.

Thus, along with the point symmetry elements and translational symmetry, the lattice has other symmetry elements, viz. the screw axes and mirror slip planes. The set of all symmetry elements of a **lattice** is called its **space group**. It was shown by E.S. Fedorov that there can be 230 space groups altogether. These groups are called the **Fedorov groups**. Not all of them were found in natural crystals. The crystals for 177 Fedorov groups have been found so far. For greater detail, we refer the reader to textbooks on crystal physics.

CRYSTALLOGRAPHIC SYSTEMS OF COORDINATES. For the coordinate systems in which the positions of lattice atoms are specified, we use rectangular coordinate systems whose

Table 5
Characteristics of Crystal Systems

Crystal system	Relation between edges of unit cell	Relation between angles in unit cell
Triclinic	$a_1 \neq a_2 \neq a_3$	$\alpha \neq \beta \neq \gamma$
Monoclinic	$a_1 \neq a_2 \neq a_3$	$\alpha = \beta = 90^\circ \neq \gamma$
Rhombic	$a_1 \neq a_2 \neq a_3$	$\alpha = \beta = \gamma = 90^\circ$
Tetragonal	$a_1 = a_2 \neq a_3$	$\alpha = \beta = \gamma = 90^\circ$
Cubic	$a_1 = a_2 = a_3$	$\alpha = \beta = \gamma = 90^\circ$
Rhombohedral	$a_1 = a_2 = a_3$	$\alpha = \beta = \gamma$, but $< 120^\circ$ and $\neq 90^\circ$
Hexagonal	$a_1 = a_2 \neq a_3$	$\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$

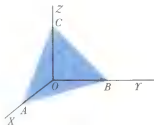


Fig. 107. To the definition of the Miller indices of the planes

axes coincide with the edges of the Bravais parallelepiped and the origin is at one of the lattice sites. The length of the corresponding edge of the Bravais parallelepiped is chosen as a unit length along each axis. Hence, the coordinates of atoms are expressed by integers. Such coordinate systems are called *crystallographic*. The choice of the coordinate axes is indicated in Table 5. The coordinate systems are rectangular for cubic, tetragonal, and rhombic crystals, while for other crystals they are oblique. The *X*- and *Y*-axes of the Bravais parallelepiped in hexagonal crystals are the sides of the regular hexagon in the base (see Fig. 105), forming the angle of 120° with each other, while the *Z*-axis is directed normally to the base. The choice of the Bravais parallelepiped for monoclinic and triclinic crystals is ambiguous. It is assumed that the axis forming right angles with two other axes is the *Z*-axis for monoclinic crystals (see Table 5).

NOTATION FOR ATOMIC PLANES. An infinite number of planes can be drawn in a crystal, each plane containing an infinite number of atoms. In order to characterize the family of parallel planes, it is sufficient to define one of them. Without loss of generality, we can confine ourselves to primitive lattices only.

In rectilinear (but not necessarily rectangular!) coordinate system, the equation of a plane has the form

$$x/|OA| + y/|OB| + z/|OC| = 1, \quad (43.6)$$

where $|OA|$, $|OB|$, and $|OC|$ are the lengths (in units of the axis) of segments intercepted by the plane on the axes of coordinates (Fig. 107). If there is an atom at the point of intersection of an axis with the plane, the corresponding value of A , B , or C is integral. But, generally speaking, the atomic plane may intersect the coordinate axes at a point where there is no atom. In this case, the corresponding value of $|OA|$, $|OB|$, and $|OC|$ will not be integral. However, it is always expressed by a rational (positive or negative) number. In order to prove this, it is sufficient to note that the quantities x , y , and z appearing in Eq. (43.6) and corresponding to atoms in the plane under consideration are integral. Hence, taking any three specific atoms in planes not lying on a straight line, we obtain from (43.6) three linear equations with integral coefficients, that can be used for finding three unknowns ($1/|OA|$, $1/|OB|$, and $1/|OC|$). The solution of these equations is obviously given by rational numbers. Consequently, $|OA|$, $|OB|$, and $|OC|$ are rational numbers. Thus, Eq. (43.6) can be rewritten in the form

$$hx + ky + lz = D, \quad (43.7)$$

where h , k , and l are integers. We can assume that these numbers have no common factor since otherwise all the terms of this equation could be divided by this common factor. The integers h , k , and l unambiguously define the position of the plane. They are called **Miller indices** and are written in the form of a sequence of numbers in parentheses: (hkl) . If an index has a negative value, the minus sign is put above the corresponding number, e.g. $(\bar{h}\bar{k}\bar{l})$.

NOTATION FOR DIRECTIONS. The direction perpendicular to a plane characterized by the Miller indices (hkl) is denoted by the same numbers in brackets: $[hkl]$.

Sec. 44. DEFECTS OF CRYSTAL LATTICES

Various types of crystal defects and their influence on the properties of solids are considered.

DEFINITION. By defects in a crystal lattice we mean any deviations from the strict periodicity which characterizes the lattice. Defects can be **macroscopic** or **microscopic**. The defects of the first type include all kinds of cracks, macroscopic cavities and various macroscopic inclusions in the crystal lattice. The defects of the second type are due to microscopic deviations from periodicity. They can be either point defects or line defects (dislocations).

POINT DEFECTS. There are three types of these defects: (1) a vacancy formed when an atom is missing from the lattice site (Schottky defect) (Fig. 108); (2) substitution by a foreign atom at the lattice site (Fig. 109); and (3) interstitial, i.e. atoms between lattice sites (Frenkel defect) (Fig. 110).

A typical feature of point defects is that they violate just the short-range order and do not disturb the long-range order.

DISLOCATIONS. Unlike point defects, line defects violate the long-range order. Dislocations disturb the regular alteration of atomic planes. They can be of **edge** or **screw** type.



Fig. 108. Vacancy



Fig. 109. Substitution



Fig. 110. Interstitial

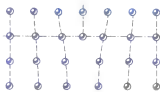


Fig. 111. Edge dislocation

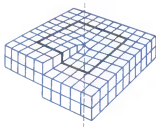


Fig. 112. Screw dislocation

An edge dislocation corresponds to an extra atomic half-plane introduced between atomic planes in a crystal (Fig. 111).

A screw dislocation is formed as a result of slip of two atomic half-planes by a period with respect to one another starting from a certain line. Figure 112 shows the lattice atoms in planes that have slipped with respect to one another. The dashed line demarcates the half-plane with slip from that without slip. Dislocations are important for studying the mechanical properties of solids.

Sec. 45. MECHANICAL PROPERTIES OF SOLIDS

Various types of deformations in solids and the relations between parameters characterizing them are considered. Plastic deformation, creep, and ultimate strength are discussed. Molecular mechanism of strength is analyzed.

DEFORMATIONS. In spite of a large variety of possible strains, they can all be reduced to two elementary strains: **uniform tension (compression) and shear.**

Tensile (compressive) strain is characterized by the relative elongation of the strained region (Fig. 113):

$$\varepsilon = (l_1 - l)/l = \Delta l/l. \quad (45.1)$$

For $\varepsilon > 0$ we have elongation, while for $\varepsilon < 0$ compression takes place.

Shear strain is characterized by the relative shear (Fig. 114a):

$$\gamma = \tan \alpha = |AB|/|OA|. \quad (45.2)$$

One of the directions of shear is conventionally considered positive and the opposite direction negative.

Any deformation is characterized by three elongations along three coordinate axes and by three shears parallel to three coordinate planes, i.e. by six quantities altogether.

All other types of deformation can be expressed in terms of these two elementary strains. For example, bending (Fig. 115) is a combination of nonuniform tension and compression. The dashed line on the figure denotes the line along which there is no strain. Torsion is reduced to a nonuniform shear strain (Fig. 116).

STRAIN TENSOR. The six quantities that describe an arbitrary strain vary from point to point. The set of these quantities constitutes the strain tensor.

In order to find the expression for this tensor, let us consider a deformed body. As a result of strain, a point of the



Fig. 113. Relative elongation

body with radius vector r shifts to a point r' , i.e. the displacement vector of this point is equal to $r' - r$, while the displacement components along the coordinate axes are equal to $u_i = x'_i - x_i$, where we put $x_1 = x$, $x_2 = y$, $x_3 = z$. If the distance between certain two points before deformation was $dl = \sqrt{dx_1^2 + dx_2^2 + dx_3^2}$ after deformation it will be equal to $dl' = [(dx_1 + du_1)^2 + (dx_2 + du_2)^2 + (dx_3 + du_3)^2]^{1/2}$. In subsequent transformations, it will be convenient to use the rule of summation over repeating indices:

$$dl'^2 = (dx_\alpha + du_\alpha)^2 = dx_\alpha^2 + 2dx_\alpha du_\alpha + du_\alpha^2 \\ = dl^2 + 2dx_\alpha du_\alpha + du_\alpha^2. \quad (45.3)$$

Considering that

$$du_\alpha = (\partial u_\alpha / \partial x_\beta) dx_\beta, \quad (45.4)$$

we give Eq. (45.3) the form

$$dl'^2 = dl^2 + 2 \frac{\partial u_\alpha}{\partial x_\beta} dx_\beta dx_\alpha + \frac{\partial u_\gamma}{\partial x_\alpha} \frac{\partial u_\gamma}{\partial x_\beta} dx_\beta dx_\alpha. \quad (45.5)$$

Since summation in formula (45.5) is performed over indices α , β , and γ , they are dummy indices and can be replaced by any others. In particular, it is obvious that

$$\frac{\partial u_\alpha}{\partial x_\beta} dx_\beta dx_\alpha = \frac{\partial u_\beta}{\partial x_\alpha} dx_\alpha dx_\beta. \quad (45.6)$$

Hence, formula (45.5) becomes

$$dl'^2 = dl^2 + 2u_{\alpha\beta} dx_\alpha dx_\beta, \quad (45.7)$$

where

$$u_{\alpha\beta} = \frac{1}{2} \left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha} + \frac{\partial u_\gamma}{\partial x_\alpha} \frac{\partial u_\gamma}{\partial x_\beta} \right) \quad (45.8)$$

Fig. 114. Relative shear (a); shear as combination of bulk compression and extension (b)

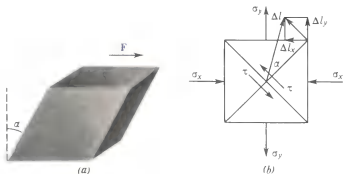




Fig. 115. Bending as a combination of nonuniform extension and compression



Fig. 116. Torsion as a nonuniform shear

is the strain tensor. It is symmetric ($u_{\alpha\beta} = u_{\beta\alpha}$), and hence contains only six different quantities.

It is known that a symmetric tensor can be reduced to the principal axes, thus giving it a diagonal form. Clearly, tensor $u_{\alpha\beta}$ can also be reduced to the principal axes. In this case, only the diagonal elements u_{11} , u_{22} and u_{33} will differ from zero, and formula (45.7) can be written in the form

$$dl^2 = (1 + 2u_{11})dx_1^2 + (1 + 2u_{22})dx_2^2 + (1 + 2u_{33})dx_3^2, \quad (45.9)$$

i.e. the strain is reduced to simple compression (or tension) along three independent mutually perpendicular directions which coincide with principal axes. For example, the length dx_1 along the X_1 -axis becomes equal to $dx_1' = dx_1\sqrt{1 + 2u_{11}}$, and so on. As we move from point to point, the direction of principal axes changes, and therefore the strain tensor is generally nondiagonal for a fixed direction of axes. Hence, the strain cannot be represented as a combination of independent compressions or tensions in these three invariable directions.

In most of the practically important cases, strains are small, i.e. $|u_{\alpha\beta}| \ll 1$. Under these conditions, the third term in the parentheses in (45.8) can be ignored in comparison with the first two terms as a quantity of the second order of smallness. Thus, we can assume that

$$u_{\alpha\beta} = \frac{1}{2} \left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha} \right). \quad (45.10)$$

According to (45.9), the relative elongation along the first principal axis is equal to

$$\epsilon_1 = \frac{dx_1\sqrt{1 + 2u_{11}} - dx_1}{dx_1} \approx u_{11}, \quad (45.11)$$

where $\sqrt{1 + 2u_{11}} \approx 1 + u_{11}$ for $|u_{11}| \ll 1$.

Similarly, the relative elongations along the two other axes are given by

$$\epsilon_2 \approx u_{22}, \quad \epsilon_3 \approx u_{33}. \quad (45.12)$$

As a result of deformation, a certain volume $dV = dx_1 dx_2 dx_3$ becomes

$$\begin{aligned} dV' &= dx_1\sqrt{1 + u_{11}} dx_2\sqrt{1 + 2u_{22}} dx_3\sqrt{1 + 2u_{33}} \\ &= dx_1 dx_2 dx_3 (1 + u_{11})(1 + u_{22})(1 + u_{33}) \\ &= dV(1 + u_{11} + u_{22} + u_{33}), \end{aligned} \quad (45.13)$$

and hence the relative change in the volume is

$$(dV' - dV)/dV = u_{11} + u_{22} + u_{33} = u_{xx}, \quad (45.14)$$

i.e. it is equal to the sum of diagonal elements of the strain tensor.

ELASTIC STRESS. Experiments show that the relative elongation ε is proportional to the force and inversely proportional to the area of the cross section to which the tensile or compressive force is applied (see Fig. 113):

$$\varepsilon = \frac{1}{E} \frac{F}{S}. \quad (45.15)$$

Here the proportionality factor is written in the form $1/E$ (E is Young's modulus), the force F acts along the normal to the surface S , and $F/S = \sigma$ is the normal stress. Then formula (45.15) can be written in the form

$$\sigma = E\varepsilon \quad (45.16)$$

and gives the value of the normal stress as a function of the relative elongation. The sign of σ is determined by the sign of ε . Similarly (see Fig. 114), for shear strain we have

$$\gamma = F/(GS), \quad (45.17)$$

where G is the shear modulus, F is the tangential force directed along the tangent to the surface, and $F/S = \tau$ is the tangential stress. Formula (45.17) can then be written in the form

$$\tau = G\gamma. \quad (45.18)$$

The quantity $1/G$ is called the shear coefficient.

POISSON'S RATIO. In uniaxial tension (compression), the change in the length of a rod is accompanied by a change in its cross-sectional area: it decreases during tension and increases upon compression. The relative change in the transverse dimension is determined by the relation

$$\varepsilon_{\perp} = \Delta l_{\perp} / l_{\perp}, \quad (45.19)$$

where $l_{\perp}$ and $\Delta l_{\perp}$ are some linear transverse dimensions of the rod and its elongation respectively. The quantity

$$\mu = -\frac{\varepsilon_{\perp}}{\varepsilon} = -\frac{(\Delta l_{\perp}/l_{\perp})}{(\Delta l/l)} \quad (45.20)$$

is called the **Poisson ratio**. The minus sign takes into account the fact that the transverse dimensions of a body decrease in tension and increase upon compression. The **Poisson ratio** characterizes the change in the volume upon a **unilateral compression or tension**.

Suppose we have a right square cylinder of the volume $V = l l_{\perp}^2$. The volume of the body after tension will be

$$V_1 = l(1 + \varepsilon) l_{\perp}^2(1 + \varepsilon_{\perp})^2 = V(1 + \varepsilon + 2\varepsilon_{\perp}), \quad (45.21)$$

where we disregarded the second-order terms in ε and $\varepsilon_{\perp}$, i.e. the terms of the second order of smallness. It follows from (45.21) that

$$(V_1 - V)/V = \Delta V/V = \varepsilon + 2\varepsilon_{\perp} = \varepsilon(1 - 2\mu). \quad (45.22)$$

The volume of the body increases upon tension and decreases upon compression. Consequently, ΔV and ε in (45.22) have the same sign, and hence

$$1 - 2\mu > 0, \quad \mu < 1/2. \quad (45.23)$$

Thus, the maximum value of the Poisson ratio is equal to $\mu_{\max} = 1/2$. In this case, the volume of the body does not change upon a unilateral tension or compression, since the change in the volume due to tension (compression) in one direction is compensated by the change in the volume due to the change in linear dimensions in perpendicular directions. The Poisson ratio lies between 0.30 and 0.40 for most of bodies.

Obviously, shear strain is not accompanied by a change in the volume.

UNIFORM TENSION OR COMPRESSION. If a body is subjected to a uniform compression, the relative change in volume, $\Delta V/V$, is proportional to the applied stress σ :

$$\frac{\Delta V}{V} = \frac{1}{\mathcal{K}} \sigma, \quad (45.24)$$

where $\mathcal{K}$ is the **bulk modulus**, and $1/\mathcal{K} = \kappa$ is the **compressibility**. In the case of solids, large stresses are required to cause an appreciable change in the volume, i.e.

compressibilities are extremely small (of the order of 10^{-11} Pa^{-1}).

Clearly, uniform compression is equivalent to a compression along the three coordinate axes. However, we must take into consideration that in accordance with (45.20), the relative elongation, say, along the X -axis is due both to the action of stresses along the X -axis and to elongations along this axis as a result of stresses along the Y - and Z -axes. Denoting the relative elongations along the axes as ε_x , ε_y , and ε_z , we can write

$$\begin{aligned}\varepsilon_x &= \sigma_x/E - \mu\varepsilon_y - \mu\varepsilon_z = [\sigma_x - \mu(\sigma_y + \sigma_z)]/E, \\ \varepsilon_y &= \sigma_y/E - \mu\varepsilon_x - \mu\varepsilon_z = [\sigma_y - \mu(\sigma_x + \sigma_z)]/E, \\ \varepsilon_z &= \sigma_z/E - \mu\varepsilon_x - \mu\varepsilon_y = [\sigma_z - \mu(\sigma_x + \sigma_y)]/E.\end{aligned}\quad (45.25)$$

These formulas can be considerably simplified for the case of uniform bulk compression when $\sigma_x = \sigma_y = \sigma_z = \sigma$:

$$\varepsilon_x = (1 - 2\mu)\sigma/E, \quad \varepsilon_y = (1 - 2\mu)\sigma/E, \quad \varepsilon_z = (1 - 2\mu)\sigma/E. \quad (45.26)$$

Thus, in bulk compression (tension) the relative elongation in a given direction differs from the elongation for unilateral compression (tension) under the action of the same stress.

RELATION BETWEEN THE BULK MODULUS AND YOUNG'S MODULUS. The relative change in the volume upon bulk compression (tension) also differs from that upon unilateral compression. For a right parallelepiped of volume $V = l_x l_y l_z$ we have for uniform bulk compression ($\sigma_x = \sigma_y = \sigma_z = \sigma$)

$$\begin{aligned}\Delta \ln V &= \Delta (\ln l_x + \ln l_y + \ln l_z) = \frac{\Delta l_x}{l_x} + \frac{\Delta l_y}{l_y} + \frac{\Delta l_z}{l_z} \\ &= \varepsilon_x + \varepsilon_y + \varepsilon_z = \frac{3(1 - 2\mu)}{E} \sigma.\end{aligned}\quad (45.27)$$

This means that the bulk modulus $\mathcal{K}$ is connected with Young's modulus E through the relation

$$\mathcal{K} = E/[3(1 - 2\mu)]. \quad (45.28)$$

RELATION BETWEEN THE SHEAR MODULUS AND YOUNG'S MODULUS. In the case of a pure shear, the volume remains unchanged. Hence, the following relation

must be observed:

$$\Delta V/V = \varepsilon_x + \varepsilon_y + \varepsilon_z = 0, \quad (45.29)$$

which can be reduced with the help of (45.25) to the form

$$\Delta V/V = (1 - 2\mu)(\sigma_x + \sigma_y + \sigma_z)/E = 0. \quad (45.30)$$

Thus, pure shear is realized only when the following relation is observed between stresses along the coordinate axes:

$$\sigma_x + \sigma_y + \sigma_z = 0. \quad (45.31)$$

Using (45.31), relations (45.25) are transformed as follows:

$$\varepsilon_x = (1 + \mu)\sigma_x/E, \quad \varepsilon_y = (1 + \mu)\sigma_y/E, \quad \varepsilon_z = (1 + \mu)\sigma_z/E. \quad (45.32)$$

In order to connect these quantities with shear, let us consider how the latter appears as a result of a combination of compressions and extensions. Figure 114b illustrates the case $\sigma_z = 0$, i.e. when the shear occurs in a plane perpendicular to the plane of the figure. From (45.31), it follows that

$$\sigma_x = -\sigma_y. \quad (45.33)$$

This means that if compression takes place along the X -axis, extension occurs along the Y -axis. If we consider a square $l_x = l_y = l$, then $|\Delta l_x| = |\Delta l_y|$ (see Fig. 114b). Consequently, the shear is parallel to the diagonal of the square. It can be seen (see Fig. 114b) that

$$\begin{aligned} \gamma &= \frac{\Delta l}{(l/\sqrt{2})} = \frac{\sqrt{(\Delta l_x)^2 + (\Delta l_y)^2}}{(l/\sqrt{2})} = \sqrt{2} \sqrt{\left(\frac{\Delta l_x}{l_x}\right)^2 + \left(\frac{\Delta l_y}{l_y}\right)^2} \\ &= \sqrt{2} \sqrt{\varepsilon_x^2 + \varepsilon_y^2} = \sqrt{2} \frac{1 + \mu}{E} \sqrt{\sigma_x^2 + \sigma_y^2}. \end{aligned} \quad (45.34)$$

The resultant of the normal stresses σ_x and σ_y is a shear stress τ acting along the diagonal (see Fig. 114b). Since the length of the diagonal is $L = \sqrt{2}l$, we immediately obtain for the shear stress

$$\tau = \sqrt{\sigma_x^2 + \sigma_y^2} / \sqrt{2} \quad (45.35)$$

and formula (45.34) assumes the form

$$\gamma = 2(1 + \mu)\tau/E. \quad (45.36)$$

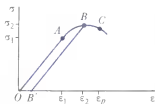


Fig. 117. Stress-strain diagram. The region of elastic ($0, \epsilon_1$), plastic (ϵ_1, ϵ_2) deformation and yield ($\epsilon > \epsilon_2$). In the latter region the material undergoes destruction

Comparing this formula with (45.18), we obtain the required relation between the shear modulus and Young's modulus:

$$G = E/[2(1 + \mu)], \quad (45.37)$$

which also involves the Poisson ratio.

Since Poisson's ratio μ is of the order of unity, the quantities G and E have approximately the same order of magnitude.

The shear modulus and Young's modulus for solids are of the order of 10^{10} – 10^{11} Pa. For example, for steel $E = 2.2 \times 10^{11}$ Pa, $G = 0.8 \times 10^{11}$ Pa; for copper $E = 1.2 \times 10^{11}$ Pa, $G = 0.44 \times 10^{11}$ Pa, for lead $E = 1.6 \times 10^{10}$ Pa, $G = 0.6 \times 10^{10}$ Pa. Thus, the values for lead are an order of magnitude lower than for steel.

PLASTIC DEFORMATION. After the stresses causing a deformation are removed, a body completely restores its original shape and volume although with a certain delay (relaxation time). Consequently, the deformation is reversible. The strain depends linearly on the stress (region OA in Fig. 117). Such deformations are called **elastic**.

The maximum value of stress σ_1 up to which deformations remain elastic is called the **elastic limit**.

If the stress is increased beyond this limit, the strain increases more rapidly than the stresses (region AB). After the stress is removed, the body does not regain its original shape and size, but shows a residual deformation (region OB'). Thus, the region of elastic deformation is followed by the region of irreversible deformation, which is known as **plastic deformation**.

YIELD. At the boundary of the plastic deformation region (point B) a situation may arise when the strain grows at a constant stress (region BC). This region is called the **yield region**, and the stress at which the material "yields" is called the **yield point**. The yield region does not always exist. Beyond the yield region, after the point C (or point B if the yield is missing) the behaviour of the σ versus ϵ curve may be quite diverse. In all cases, however, at a certain stress a limit is attained after which the material breaks down.

ULTIMATE STRENGTH. The stress at which the material fails is called the **ultimate strength**.

Substances for which the elastic limit and ultimate strength are close and the yield region is practically missing are called **brittle**. These materials fail almost immediately after the elastic limit (as in the case of cast iron or tempered steel).

If after undergoing plastic deformation, a material is deformed again, the deformation will be elastic, the elastic limit being usually higher than in the previous deformation (region AB). Even σ_2 , i.e. the upper limit of the previous region of plastic deformation, can now be the elastic limit. It can be stated that plastic deformation has made the material stronger. There are other methods of strengthening materials, for example, tempering or strengthening with the help of forcing impurities, i.e. alloying. Tempering consists in rapid cooling of a metal heated to a high temperature by submerging it into water or oil.

MOLECULAR MECHANISM OF STRENGTH. Clearly, deformations cause a change in the mutual arrangement of lattice atoms and the distance between them.

The stresses appearing in this case are manifestations of the forces of intermolecular interaction in their nature. Experimental studies and theoretical calculations show that the elastic limit of real crystals is considerably lower than for ideal crystals.

This leads to a conclusion that the role of crystal lattice defects in its strength is very important. It was found that dislocations play the decisive role. Dislocations move as a result of deformations, and the strength of a material is determined mainly by the ease with which dislocations move.

The factors that hamper the movement of dislocations improve the strength of a material. In particular, strengthening caused by plastic deformation can be explained by an increase in the number of dislocations, as a result of which their mobility decreases, and, therefore, the material is strengthened.

Impurities also usually hamper the movement of dislocations, i.e. increase the strength of materials.

However, the strength of a material can be increased many times if lattice defects are eliminated. In this case, in particular, dislocations will also disappear in the crystal, and we cannot speak of their movement. Such an increase in the strength of materials having an ideal crystal lattice was confirmed in experiments. However, the production of materials with a crystal lattice without defects is extremely difficult.

Sec. 46. HEAT CAPACITY OF SOLIDS

The Einstein and Debye theories of heat capacities and the conditions of their applicability are considered. The formula for heat capacity is derived by using the concept of phonons.

CLASSICAL THEORY. A crystalline solid whose atoms vibrate near equilibrium positions at the lattice sites is used as a model. Each atom can vibrate independently in three mutually perpendicular directions and is a linear oscillator with respect to each of these directions. In accordance with the law of equipartition of energy, each oscillator has a vibrational energy equal to kT , which consists of kinetic and potential energies equal to $kT/2$ each.

Thus, as a result of thermal motion, a body consisting of n atoms has the energy

$$U = 3nkT, \quad (46.1)$$

while its heat capacity is equal to

$$C_V = (\partial U / \partial T)_V = 3nk, \quad (46.2)$$

i.e. the heat capacity of a solid is constant. If we take one mole of molecules of a substance, n will be equal to the Avogadro constant N_A , and $nk = R$, the molar gas constant. Formula (46.2) shows that the molar heat capacity is equal to $3R$ and is independent of temperature. This is the law of Dulong and Petit.

HEAT CAPACITY AT LOW TEMPERATURES. Experiments on measurement of heat capacity at low temperatures have shown that, as in the case of gases (see Sec. 17), it depends on temperature. As the temperature approaches 0 K, the heat capacity tends to zero in accordance with the power law $C_V \propto T^3$. The experimentally obtained temperature dependence of the heat capacity is depicted in Fig. 118. It should be noted that such a dependence of heat capacity on temperature is observed only for nonmetallic solids whose only energy associated with thermal motion is the energy of atomic vibrations at the lattice sites. In metals, free electrons take part in thermal motion and contribute to the heat capacity. However, this contribution is small since only a small number of electrons whose energy is close to the energy of the Fermi surface participate in thermal motion. The electron heat capacity plays a major role only when the temperature is low, and the main heat capacity becomes very small.

EINSTEIN'S MODEL. In order to explain the temperature dependence of heat capacity, Einstein proposed (1907) that we should take into consideration the discrete nature of energies that the oscillators forming a solid may assume, as it was done earlier by M. Planck while deriving the formula for the black-body radiation.

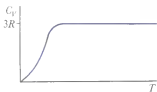


Fig. 118. Temperature dependence of the heat capacity for nonmetallic solids

Let ε be the “elementary” portion of energy which a linear oscillator may possess. This energy can be assumed to be connected with a certain frequency of the oscillator through the same relation that connects the photon energy with its frequency:

$$\varepsilon = \hbar\omega. \quad (46.3)$$

Generally speaking, we cannot state that the minimum energy of an oscillator is equal to zero. Let us denote this energy by ε_0 . The exact value of this energy is not important for calculating the heat capacity. Hence the possible energies that the oscillator may have can be represented in the form

$$\varepsilon_n = \varepsilon_0 + n\varepsilon \quad (n = 0, 1, 2, \dots). \quad (46.4)$$

It is natural to assume that the probability $\mathcal{P}_n$ of the state of the oscillator with energy ε_n is given by Boltzmann’s formula. Hence we can write

$$\mathcal{P}_n = A \exp[-\varepsilon_n/(kT)] = A \exp[-(\varepsilon_0 + n\varepsilon)/(kT)], \quad (46.5)$$

where A is a normalized constant determined by the normalization condition for probability:

$$\sum_{n=0}^{\infty} \mathcal{P}_n = \exp[-\varepsilon_0/(kT)] A \sum_{n=0}^{\infty} \exp[-n\varepsilon/(kT)] = 1. \quad (46.6)$$

We can now calculate the mean energy of the oscillator:

$$\begin{aligned} \langle \varepsilon \rangle &= \sum_{n=0}^{\infty} \varepsilon_n \mathcal{P}_n \\ &= \varepsilon_0 + \varepsilon \sum_{n=0}^{\infty} n \exp[-n\varepsilon/(kT)] / \sum_{n=0}^{\infty} \exp[-n\varepsilon/(kT)]. \end{aligned} \quad (46.7)$$

The formula for geometric progression gives

$$\sum_{n=0}^{\infty} \exp[-n\varepsilon/(kT)] = \{1 - \exp[-\varepsilon/(kT)]\}^{-1}. \quad (46.8)$$

Differentiating both sides of this equation with respect to ε , we obtain

$$\begin{aligned} &\sum_{n=0}^{\infty} n \exp[-n\varepsilon/(kT)] \\ &= \exp[-\varepsilon/(kT)] \{1 - \exp[-\varepsilon/(kT)]\}^{-2}. \end{aligned} \quad (46.9)$$

Consequently, the relation (46.7) becomes

$$\langle \varepsilon \rangle = \varepsilon_0 + \frac{\varepsilon}{\exp [\varepsilon / (kT)] - 1}. \quad (46.10)$$

Hence we obtain the following expression for the vibrational energy of one mole of oscillators:

$$U = 3N_A \langle \varepsilon \rangle = 3N_A \varepsilon_0 + \frac{3N_A \varepsilon}{\exp [\varepsilon / (kT)] - 1}. \quad (46.11)$$

Then the heat capacity at constant volume is given by

$$\begin{aligned} C_V &= \left(\frac{\partial U}{\partial T} \right)_V \\ &= 3N_A k \left(\frac{\varepsilon}{kT} \right)^2 \exp [\varepsilon / (kT)] / \{ \exp [\varepsilon / (kT)] - 1 \}^2. \end{aligned} \quad (46.12a)$$

This is the Einstein formula for heat capacity. The behaviour of heat capacity dependence on temperature described by this formula is qualitatively in good agreement with the experimental results presented in Fig. 118. Indeed, formula (46.12a) shows that for a sufficiently high temperature ($T \rightarrow \infty$) $C_V \rightarrow 3R$, while for $T \rightarrow 0$ we obtain

$$C_V \rightarrow 3R [\varepsilon / (kT)]^2 \exp [-\varepsilon / (kT)] \rightarrow 0.$$



The motion of system of coupled oscillators is described by taking into account the normal vibrational modes of the system. In this case, the energy is carried not by individual oscillator but by a normal vibrational mode of the system as a whole, which is considered as a quasiparticle called the phonon.

Phonons and other quasiparticles that are normal modes of corresponding excitations (magnons, polarons, excitons, etc.) are not particles in the same sense as photons, although the mathematical algorithms for describing their behaviour may have much in common.

EINSTEIN'S TEMPERATURE. The "elementary portion of energy" ε depends on the material properties of a solid. This quantity increases with "hardness" of the material, since in this case the vibrational frequency ω in formula (46.3) increases. This energy is usually characterized in terms of the Einstein temperature Θ_E defined by the relation

$k\Theta_E = \varepsilon.$

$$(46.12b)$$

Formula (46.12a) can then be rewritten as

$$C_V = \frac{3R (\Theta_E/T)^2 \exp (\Theta_E/T)}{[\exp (\Theta_E/T) - 1]^2}. \quad (46.12c)$$

INSUFFICIENCY OF EINSTEIN'S THEORY. However, formula (46.12a) does not quantitatively agree with experimental

results, since it predicts an exponential decrease in the heat capacity $C_V \propto \exp[-\varepsilon/(kT)]$ as we approach 0 K, while the experiments give a decrease only in accordance with the power law $C_V \propto T^3$.

Thus, Einstein's model is unsuitable for calculating the heat capacity and must be replaced by some other model. Besides the quantitative discrepancy between the calculated and experimental results, there is another serious drawback in this theory. It is assumed that a solid is a system of independent linear oscillators whose energies are given by formula (46.4), i.e. the movements of atoms in the solid are assumed to be independent of each other as the motions of atoms and molecules in gases. But this is known to be wrong, since the confinement of atoms near certain equilibrium positions is itself the result of interaction between the atoms. Therefore atoms in a solid cannot be assumed to be independent; we must take into account their cooperative interactions. Taking this interaction into consideration, we arrive at a theory of heat capacity that is in agreement with experimental results.

ELEMENTARY EXCITATIONS. At 0 K, the system of atoms comprising a solid is in the ground state having the minimum energy. In order to investigate the heat capacity in the vicinity of 0 K, we must specify the energies the system may have at temperatures close to 0 K. Suppose that after receiving an energy from outside, an atom moves in a certain direction from its equilibrium position. The force striving to return it to the equilibrium position is just the repulsive force exerted on it by other lattice atoms. Therefore, while leaving the equilibrium position, the atom acts with a certain force on neighbouring atoms which in turn are to leave their equilibrium positions, as a result of which the motion becomes cooperative. This cooperative motion, when the displacement of one atom is transferred to the neighbouring atom, and then to the next neighbour, and so on, is nothing but an acoustic wave in a solid. Thus, elementary excitations are acoustic vibrations.

NORMAL MODES. Taking into account the interaction described above, a system of atoms must be considered as a set of coupled oscillators. In this case, any motion of the system of atoms can be represented as a superposition of normal oscillations, or normal modes of the system. Each of the normal modes is characterized, in addition to other parameters, by its frequency, and the energy of this mode is given by formula (46.3), i.e. a mode with frequency ω_i has the energy

$$\varepsilon_i = \hbar\omega_i, \quad (46.13)$$

where the energy ε_0 , which is the same for all modes, is discarded. One, two, or more oscillations of a given mode can be excited in a solid. If n oscillations of a given mode are excited, the total energy of these n oscillations is obviously equal to

$$\varepsilon_{in} = n\hbar\omega_i. \quad (46.14)$$

The probability that the total energy ε_{in} corresponds to a given mode is assumed to obey the Boltzmann distribution, and hence

$$\mathcal{P}_{in} = A \exp[-\varepsilon_{in}/(kT)] = A \exp[-n\hbar\omega_i/(kT)], \quad (46.15)$$

where A is the normalization factor. This formula is similar to (46.5). It can be used to calculate the mean energy per mode under consideration. By dividing this energy into the energy of one oscillation of the mode, we can immediately obtain the mean number $\langle n_i \rangle$ of oscillations of the given mode, excited in a system. Calculations, completely analogous in the mathematical sense to those which led to (46.10) from (46.5), give the following result:

$$\langle n_i \rangle = \frac{\langle \varepsilon_{in} \rangle}{\hbar\omega_i} = \frac{1}{\hbar\omega_i} \sum n\hbar\omega_i \mathcal{P}_{in} = \frac{1}{\exp[\hbar\omega_i/(kT)] - 1}. \quad (46.16)$$

The problem of calculating the total energy of excitation is thus reduced to determining the frequencies of normal modes and their number.

PHONONS. Expression (46.13) for the energy corresponding to the mode with frequency ω_i suggests, in analogy with the corresponding formula for the photon energy, that such a mode should be treated as a quasiparticle. Essentially, this representation has already been used in (46.15) when we applied the Boltzmann formula for determining the mean energy in a mode. Such a quasiparticle associated with the modes of acoustic oscillations is called a **phonon**. The introduction of the phonon concept is a fruitful approach which considerably simplifies the reasoning. This approach is also very effective from a mathematical point of view, since the formal mathematical methods of calculating various quantities associated with phonons are similar to the corresponding calculations for photons. This analogy is due to the fact that mathematically we are dealing with identical wave processes. The physical nature of these processes is, however, quite different. Therefore the fact that photons exist

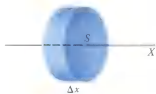


Fig. 119. To the derivation of the wave equation

as particles which have an experimentally observable energy and can exist independently does not imply that phonons are also particles with similar properties. In modern physics there is a large number of other similar quasiparticles that are normal modes of the corresponding excitations (magnons, polarons, excitons, etc.). All that has been said about phonons is also valid for these quasiparticles.

DEBYE MODEL. Longitudinal and transverse waves may propagate in a solid with different velocities. Transverse modes may have two different directions of polarization. Thus, we can simply speak about long-wave modes of acoustic waves with three different polarizations which are generally different and may depend on the direction of propagation of the wave. For the sake of simplicity, we shall consider the case of an isotropic solid. The number of modes for each polarization is calculated in the same way. The Debye theory of heat capacity is based on the calculation of the number of modes of acoustic oscillations in a solid. We must only add to what has been said above that we shall be dealing with sufficiently long-wave modes since near 0 K the excitations and oscillation frequencies must correspond to sufficiently low energies, i.e. they must be small.

DISPERSION RELATION. First of all, we shall derive the wave equation, for example, for longitudinal waves propagating along the X -axis (Fig. 119). Suppose that we have a thin cylinder with the area S of the base and height Δx . We denote the density of the substance by $\rho(x, t)$, the pressure appearing in it as a result of a change in density by $p(x, t)$, and the velocity of oscillations of particles along the X -axis by $u(x, t)$. This velocity is not equal to the velocity of propagation of the wave but is many hundreds of times lower.

We shall write the law of conservation of mass in a volume: the change in the mass in the volume per unit time $\partial(\rho S \Delta x)/\partial t$ is equal to the difference between the masses entering the volume and leaving it:

$$\begin{aligned} \frac{\partial(\rho S \Delta x)}{\partial t} &= S\rho(x, t)u(x, t) - S\rho(x + \Delta x, t)u(x + \Delta x, t) \\ &= -S\Delta x \frac{\partial(\rho u)}{\partial x}, \end{aligned} \quad (46.17)$$

where the derivative is expanded into a Taylor series and only the first term linear in Δx is retained. The remaining terms can be disregarded since we will assume that Δx is an infinitesimal. After cancelling out $S\Delta x$ from both sides of

?

1. What is the main drawback of Einstein's model for the heat capacity of a solid?
2. Why is the electron heat capacity in metals manifested only at temperatures close to 0 K?
3. What is a phonon? What other elementary excitations do you know?
4. What is the relation between the Debye temperature and the mean velocity of sound in a material?
5. Which arguments prove that the curve for heat capacity as a function of the ratio of the temperature to the Debye temperature is universal?

Eq. (46.17), we obtain the following equation:

$$\rho \frac{\partial p}{\partial t} + \frac{\partial (\rho u)}{\partial x} = 0, \quad (46.18)$$

which is called the continuity equation.

The force acting on a mass in the volume under consideration is due to the difference in pressure p on different walls of the cylinder. Consequently, the Newton equation has the form

$$\rho S \Delta x \partial u / \partial t = S p(x, t) - S p(x + \Delta x, t) = -S \Delta x \partial p / \partial x \quad (46.19)$$

or

$$\rho \frac{\partial u}{\partial t} + \frac{\partial p}{\partial x} = 0. \quad (46.20)$$

The changes in density and pressure can be considered to be small:

$$\rho = \rho_0 + \rho', \quad p = p_0 + p', \quad (46.21)$$

where ρ_0 and p_0 are the density and pressure in the medium, which are constant in the absence of a wave; ρ' and p' are the changes in density and pressure introduced by the wave. These changes are quite small. All subsequent calculations are made retaining the first-order terms in ρ' and p' .

Substituting (46.21) into Eqs. (46.18) and (46.20), and retaining only the linear terms in ρ' and p' , we get

$$\frac{\partial \rho'}{\partial t} + \rho_0 \frac{\partial u}{\partial x} = 0, \quad \rho_0 \frac{\partial u}{\partial t} + \frac{\partial p'}{\partial x} = 0. \quad (46.22)$$

These two equations are insufficient for determining three unknowns ρ' , p' , and u . One more equation containing these quantities is required. This is the equation of state, connecting pressure and density:

$$p = p(\rho). \quad (46.23)$$

Taking this equation into account, we obtain from (46.21)

$$p_0 + p' = p(\rho_0) + \rho' \frac{\partial p(\rho_0)}{\partial \rho}, \quad (46.24)$$

i. e.

$$p' = \rho' \frac{\partial p}{\partial \rho} = \rho' v^2, \quad (46.25)$$

$\omega = \pm vk$

where

$$\frac{\partial p}{\partial \rho} = v^2. \quad (46.26)$$

It will be shown later that v is the velocity of propagation of waves.

Using Eq. (46.25), we can eliminate p' from Eqs. (46.22). As a result, these equations become

$$\frac{\partial \rho'}{\partial t} + \rho_0 \frac{\partial u}{\partial x} = 0, \quad \rho_0 \frac{\partial u}{\partial t} + v^2 \frac{\partial \rho'}{\partial x} = 0. \quad (46.27)$$

Differentiating the first of these equations with respect to t and the second with respect to x , and subtracting the first equation from the second one, we obtain

$$\frac{\partial^2 \rho'}{\partial x^2} - \frac{1}{v^2} \frac{\partial^2 \rho'}{\partial t^2} = 0. \quad (46.28)$$

Similarly, differentiating the first of Eqs. (46.27) with respect to x and the second with respect to t , and subtracting them termwise, we get

$$\frac{\partial^2 u}{\partial x^2} - \frac{1}{v^2} \frac{\partial^2 u}{\partial t^2} = 0. \quad (46.29)$$

Equations (46.28) and (46.29) describe a wave propagating along the X -axis with the velocity v . This is directly seen from the fact that any function $f(t - x/v)$ is a solution of this equation. Therefore, the wavefront $f = \text{const}$ is given by the condition

$$t - x/v = \text{const}, \quad (46.30)$$

from which it follows that

$$(dx/dt) = v, \quad (46.31)$$

i.e. v is indeed the velocity of propagation of the wavefront.

We shall seek the solution of Eqs. (46.28) and (46.29) in the following form:

$$\rho' = \rho'_0 \exp[i(\omega t - kx)], \quad u = u_0 \exp[i(\omega t - kx)]. \quad (46.32)$$

Substituting (46.32) into (46.27), we obtain the algebraic equations for determining ρ'_0 and u_0 :

$$-i\omega\rho'_0 + ik\rho_0 u_0 = 0, \quad ikv^2\rho_0 - i\omega\rho_0 u_0 = 0. \quad (46.33)$$

In order that this homogeneous system have nontrivial (nonzero) solutions for ρ'_0 and u_0 , it is necessary that the determinant composed of the coefficients of these equations be equal to zero:

$$\begin{vmatrix} i\omega & ik\rho_0 \\ ikv^2 & -i\omega\rho_0 \end{vmatrix} = \omega^2\rho_0 - k^2v^2\rho_0 = 0, \quad (46.34)$$

whence

$$\omega = \pm vk. \quad (46.35)$$

This relation connects the wave frequency $\omega = 2\pi/T$ with the wave number $k = 2\pi/\lambda$, where T and λ are the period of oscillations and the wavelength, and is called the **dispersion relation**. In the case under consideration, it has a simple form. However, in other cases it can be more complicated. This relation makes it possible to determine the oscillation frequencies, and hence the energies of the corresponding modes from the known wave numbers.

CALCULATION OF THE NUMBER OF MODES. Standing waves appear in a body of finite dimensions. The boundaries of the body freely oscillate and no stress appears on them. Suppose that we have a body in the form of a cube with volume L^3 and the origin of coordinates at one of its vertices. Let us consider plane standing waves along the X -axis. We denote by ξ the deviation of an oscillating point from the equilibrium position. Since the surface of the cube is free, no stress appears on it during oscillations, i.e. the boundary condition has the form

$$\left. \frac{\partial \xi}{\partial x} \right|_{\substack{x=0 \\ x=L}} = 0. \quad (46.36)$$

The solution of Eq. (46.29) satisfying this condition has the form

$$\xi = \exp(i\omega t) (A \sin kx + B \cos kx), \quad (46.37)$$

where ω and k are related through (46.35). In order to satisfy condition (46.36), we must put $A = 0$ in (46.37), and impose the following condition on k :

$$kL = n\pi \quad (n = 1, 2, \dots).$$

This condition determines the discrete set of wave numbers for which standing waves can exist. Similar relations can be obtained for other coordinate axes. Consequently, we get the

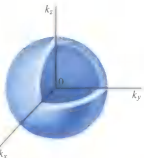


Fig. 120. Space of wave numbers

following sets of the wave numbers, each of which corresponds to a standing wave constituting a mode of oscillations:

$$k_x = \pi n_x / L \quad k_y = \pi n_y / L \quad k_z = \pi n_z / L \quad (46.38)$$

$$(n_x = 1, 2, \dots), \quad (n_y = 1, 2, \dots), \quad (n_z = 1, 2, \dots).$$

The numbers n_x , n_y , and n_z run independently through all possible values. The calculation of the number of modes is reduced to the determination of the number of different triplets of numbers (n_x, n_y, n_z) or, in other words, to the calculation of the number of points with Cartesian coordinates (n_x, n_y, n_z) .

The number of these points in a volume with side lengths Δn_x , Δn_y , and Δn_z is equal to $\Delta n_x \Delta n_y \Delta n_z$. Consequently, the number of modes corresponding to these numbers is

$$dN = \Delta n_x \Delta n_y \Delta n_z = \frac{L^3}{\pi^3} dk_x dk_y dk_z, \quad (46.39)$$

where $\Delta n_x = (L/\pi) dk_x$, etc., as it follows directly from (46.38). The right-hand side of (46.39) contains the differentials dk_x , dk_y , dk_z since L is much larger than the wavelength.

For calculating dN , it is more convenient to go over to spherical coordinates (Fig. 120), taking into account that k_x , k_y , and k_z assume only positive values. This means that in (46.39) we must put $dk_x dk_y dk_z = (4\pi/8) k^2 dk$. As a result we obtain from (46.39) the following expression for the number of modes corresponding to the wave numbers lying in the interval from k to $k + dk$:

$$dN = \frac{4\pi L^3}{(2\pi)^3} k^2 dk, \quad (46.40)$$

where we retain the factor 4π instead of cancelling it by the expression $(2\pi)^3$ in the denominator in order to emphasize the transition to spherical coordinates.

Further, we use the relation (46.35) from which it follows that

$$k^2 dk = (1/v^3) \omega^2 d\omega, \quad (46.41)$$

and hence the number of modes with oscillation frequency lying between ω and $\omega + d\omega$ is equal to

$$dN = \frac{4\pi L^3}{(2\pi)^3 v^3} \omega^2 d\omega. \quad (46.42)$$

MODE DENSITY. The number of modes divided by the frequency interval is called the **mode density**:

$$\rho(\omega) = dN/d\omega. \quad (46.43)$$

Hence it follows from (46.42) that

$$\rho(\omega) = \frac{4\pi L^3}{(2\pi)^3 v^3} \omega^2. \quad (46.44)$$

$$\rho(\omega) = \frac{4\pi L^3}{(2\pi)^3 v^3} \omega^2$$

Similar calculations can be made for each of the transverse modes. In the isotropic case, the velocities of the two transverse waves are equal. Denoting the velocities of the transverse and longitudinal modes by v_{long} and v_{tr} and taking into account that the density of all the modes is equal to the sum of the densities of individual modes, we can write

$$\rho(\omega) = \frac{4\pi L^3}{(2\pi)^3} \left(\frac{1}{v_{\text{long}}^3} + \frac{2}{v_{\text{tr}}^3} \right) \omega^2. \quad (46.45)$$

To avoid complex notations in (46.45), the total mode density is denoted by the same letter as in (46.44) for the mode density of one of the polarizations.

The above calculations imply that formula (46.45) is not valid for very short waves since we have ignored the atomic structure of a solid and performed calculations as if the mass of the solid were continuously distributed over its volume. Formula (46.45) is valid for waves whose wavelength considerably exceeds the mean distance between the atoms, and displacements of atoms from their equilibrium positions are not very large. It is just this case that is important for considering heat capacity at low temperatures.

On the other hand, since the values of temperature and kT are very small, expression (46.45) is valid up to the frequencies for which $\hbar\omega \gg kT$. In this region, the exponential $\exp[\hbar\omega/(kT)]$ appearing in the denominator of (46.16) is large, and hence the average number of modes with very high frequencies is exponentially small. This means that their contribution to the total energy is very small. Therefore, in spite of the fact that expression (46.45) does not hold for high frequencies, it can be used up to infinitely high frequencies since the exponential term will nullify the contribution from these frequencies to the quantities being calculated.

HEAT CAPACITY AT LOW TEMPERATURES. The total energy of all modes of oscillations associated with thermal energy is equal to

$$\begin{aligned}
 U &= \int_0^{\omega} \langle n(\omega) \rangle \rho(\omega) \hbar \omega d\omega \\
 &= \frac{4\pi L^3 \hbar}{(2\pi)^3} \left(\frac{1}{v_{\text{long}}^3} + \frac{2}{v_{\text{tr}}^3} \right) \int_0^{\omega} \frac{\omega^3 d\omega}{\exp[\hbar\omega/(kT)] - 1} \\
 &= \frac{4\pi L^3}{(2\pi\hbar)^3} \left(\frac{1}{v_{\text{long}}^3} + \frac{2}{v_{\text{tr}}^3} \right) (kT)^4 \int_0^{\infty} \frac{\xi^3 d\xi}{e^{\xi} - 1}. \quad (46.46)
 \end{aligned}$$

The integral contained in this expression can be evaluated by the methods of complex variable functions. It is given by

$$\int_0^{\infty} \frac{\xi^3 d\xi}{e^{\xi} - 1} = \frac{\pi^4}{15}.$$

Formula (46.46) can be used for calculating the heat capacity

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V \propto T^3. \quad (46.47)$$

Such a temperature dependence of heat capacity in the vicinity of 0 K is confirmed by experiments.

DEBYE TEMPERATURE. Strictly speaking, all the above calculations and, in particular, the derivation of the dispersion relation, are valid only for waves with sufficiently large wavelengths. Consequently, formula (46.45) obtained on the basis of the dispersion relation is also valid only for such waves, i.e. for not very high frequencies. However, the remarks about the contribution of short waves to heat capacity, made above in connection with formula (46.45), imply that we shall not make a serious mistake if we apply this formula to high frequencies also, up to the maximum frequency ω_{max} defined in such a way that the total number of modes in this case is equal to the actually available number $3N_A$ of modes. Therefore we have

$$3N_A = \int_0^{\omega_{\text{max}}} \rho(\omega) d\omega. \quad (46.48)$$

The maximum frequency ω_{max} depends on the elastic properties of the material. Generally, this frequency can be

different for different directions of polarization. For the sake of simplicity, however, a certain average maximum frequency is used in formula (46.48). Substituting (46.45) into (46.48) and integrating, we obtain

$$\omega_{\max} = 2\pi\langle v \rangle \left(\frac{3N_A}{4\pi L^3} \right)^{1/3}, \quad (46.49)$$

where $\langle v \rangle$ is the mean velocity of sound determined by the relation

$$1/v_{\text{long}}^3 + 2/v_{\text{tr}}^3 = 3/(\langle v \rangle)^3. \quad (46.50)$$

The maximum frequency determined in accordance with condition (46.48) is usually expressed in terms of the Debye temperature Θ_D obtained from the relation

$$k\Theta_D = \hbar\omega_{\max}. \quad (46.51)$$

Normally, the Debye temperature lies between 100 and 1000 K. For example, it is about 340 K for copper, while for diamond it is about 2000 K.

HEAT CAPACITY AT AN ARBITRARY TEMPERATURE. While calculating the energy U in (46.46), we did not take into account the presence of the maximum frequency $\omega_{\max}$ defined by formula (46.48). Taking this frequency into consideration, we must bound the integral by the frequency $\omega_{\max}$. Then instead of formula (46.46), we get

$$U = \frac{12\pi L^3}{(2\pi\hbar)^3 \langle v \rangle^3} \int_0^{\omega_{\max}} \frac{\omega^3 d\omega}{\exp[\hbar\omega/(kT)] - 1}, \quad (46.52)$$

where $\langle v \rangle$ is defined by relation (46.50). Going over to the dimensionless quantity

$$\xi = \hbar\omega/(kT) \quad (46.53)$$

upon integration and taking into account (46.49) and (46.51), we obtain

$$U = 9N_A kT \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{\xi^3 d\xi}{\exp \xi - 1}. \quad (46.54)$$

Differentiating this equation with respect to T , we can find the heat capacity C_V . For $T \ll \Theta_D$ the upper integration limit can be extended to ∞ which gives (46.47).

For $T \gg \Theta_D$ the upper integration limit is close to zero. Hence ξ in the integrand is a very small quantity and we can

$$\Theta_D = \hbar\omega_{\max}/k$$

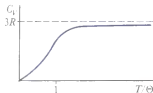


Fig. 121. The universal curve for the heat capacity of solids

assume that $\exp \xi \approx 1 + \xi$. Hence formula (46.54) becomes

$$U = 9N_A k T \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{\xi^3 d\xi}{\xi} = 3N_A k T = 3RT. \quad (46.55)$$

Consequently, the heat capacity in this case is given by

$$C_V = (\partial U / \partial T)_V = 3R, \quad (46.56)$$

i.e. it obeys the Dulong and Petit law, as expected.

For $T \sim \Theta_D$, the integral in (46.54) cannot be taken analytically and we must use numerical methods. The Debye temperature Θ_D takes into account the properties of various materials. Therefore, the curve describing the heat capacity as a function of the ratio T/Θ_D is universal. It is shown in Fig. 121 and is in excellent agreement with the experimental results shown qualitatively in the form of the curve in Fig. 118.

DERIVATION OF THE FORMULA FOR HEAT CAPACITY ON THE BASIS OF THE PHONON CONCEPTS. In order to get acquainted with the concept of quasiparticles, it is useful to derive the formula for the heat capacity of a solid on the basis of the phonon concept.

As was remarked in connection with formula (46.13), the vibrational mode corresponding to the energy $\hbar\omega$ can be considered a quasiparticle. With this approach, the thermal vibrations of a lattice are reduced to an aggregate of phonons treated as an ideal gas.

According to (46.13), the phonon energy is equal to

$$\varepsilon = \hbar\omega, \quad (46.57)$$

and its momentum p is connected with the wave number k through the conventional relation for free particles:

$$p = \hbar k. \quad (46.58)$$

The energy and momentum of a phonon are connected through relation (46.35) which, taking into account (46.57) and (46.58), can be written in the form

$$\varepsilon = \langle v \rangle p, \quad (46.59)$$

where several phonon polarizations are taken into consideration, and their average velocity is represented in accordance with (46.50).

The density of states for a gas consisting of phonons as quasiparticles is given by formula (8.4) in the form

$$d\Gamma = \rho(\varepsilon) d\varepsilon = 3V 4\pi p^2 dp / (2\pi\hbar)^3. \quad (46.60)$$

The factor 3 takes into account the three possible polarizations of phonons. Using (46.58), we obtain the following expression from (46.60):

$$\rho(\varepsilon) = \frac{12\pi V}{(2\pi\hbar)^3} \frac{1}{(\langle v \rangle)^3} \cdot \varepsilon^2. \quad (46.61)$$

In further calculations, it is convenient to express $\rho(\varepsilon)$ not through the velocity $\langle v \rangle$ of sound but in terms of the Debye temperature by using the condition that the total number of phonons must be equal to

$$3N_A = \int_0^{k\Theta_D} \rho(\varepsilon) d\varepsilon. \quad (46.62)$$

Then

$$\rho(\varepsilon) = 9N_A \varepsilon^2 / (k\Theta_D)^3. \quad (46.63)$$

Phonons are particles obeying the Bose-Einstein statistics, and hence the average number $\langle n \rangle$ of phonons having the energy ε is given by formula (28.2) which has the following form in the case under consideration:

$$\langle n(\varepsilon) \rangle = \{ \exp[\varepsilon/(kT)] - 1 \}^{-1}. \quad (46.64)$$

Thus, we obtain the following expression for the total energy of phonons in a body:

$$U = \int_0^{k\Theta_D} \varepsilon \rho(\varepsilon) \langle n(\varepsilon) \rangle d\varepsilon = 9N_A kT \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{\xi^3 d\xi}{\exp \xi - 1}, \quad (46.65)$$

which, as should be expected, coincides with formula (46.54).

The above derivation shows that the concept of quasiparticles (phonons in our case) makes it possible to use the concepts and mathematical methods elaborated for real particles. However, this does not imply that quasiparticles exist in the same sense as real particles do. For example, in the derivation of the formula for the heat capacity presented above, we treat a phonon in the same way as a photon while deriving the formula for black-body radiation in Sec. 28. Nevertheless, a phonon cannot be called ■ elementary particle in the same sense as ■ photon which is one of the basic elementary particles in physics.

HEAT CAPACITY OF METALS. In this case, the heat capacity due to thermal lattice vibrations is supplemented with the heat capacity of free electrons in a metal (see (27.21)). At normal temperatures, it constitutes a negligible part of the lattice heat capacity and need not be taken into

account. As the temperature decreases, however, the lattice heat capacity decreases in proportion to T^3 , while the electron heat capacity decreases in proportion to T . Therefore, the role of the electron heat capacity increases, and dominates over the lattice heat capacity at a sufficiently low temperature.

Example 46.1. Using the classical law of equipartition of energy, calculate the specific heat capacities for KCl and NaCl.

Since the mean kinetic energy of vibrations of an oscillator is equal to the mean potential energy, the mean energy per vibrating molecule is $\langle \epsilon \rangle = 3kT$. The number of moles in 1 kg of mass is equal to $1/M$, where M is the molar mass. Consequently, 1 kg of mass contains $n = N_A/M$ molecules, and the specific heat capacity is equal to

$$c = \partial(6kTN_A/M)/\partial T = 6kN_A/M = 6R/M.$$

Since $M_{\text{KCl}} = 0.07456$ kg/mole, and $M_{\text{NaCl}} = 0.05845$ kg/mole, we find

$$c_{\text{KCl}} = 6 \cdot 8.31/0.07456 \text{ J/(kg} \cdot \text{K)};$$

$$c_{\text{NaCl}} = 6 \cdot 8.31/0.05845 \text{ J/(kg} \cdot \text{K)}.$$

Example 46.2. Investigate the heat capacity of solids under the assumption that phonons are fermions and consequently obey the Fermi-Dirac rather than the Bose-Einstein statistics. Assume that in all other respects their properties remain the same.

Obviously, all the calculations that led to formula (46.65) remain unchanged, and only expression (46.64) for the average number of particles must be replaced by an expression corresponding to the Fermi-Dirac statistics. In other words, the minus sign in the denominator must be replaced by plus. As a result, we obtain the following expression for the total energy instead of formula (46.65):

$$U = 9N_A kT \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{\xi^3 d\xi}{\exp \xi + 1}. \quad (46.66)$$

The difference in the behaviour of heat capacity (see (46.66)) in comparison with (46.65) boils down to the following. At a very high temperature, the upper limit is low, and we can put $\exp \xi \simeq 1 + \xi$ in the integrand. In this case the heat capacity in (46.65) is constant. The heat capacity at high temperatures calculated from formula (46.66) tends to zero for fermions. As regards the heat capacity at low temperatures, it varies in proportion to T^3 .

Sec. 47. CRYSTALLIZATION AND MELTING

The physical processes of melting, crystallization, and sublimation are considered. Anomalous substances are defined. General comparative characteristics of the first- and second-order phase transitions are given.

DEFINITION. Experience shows that as the temperature is lowered at a sufficiently low pressure, all substances except liquid helium become solids, i.e. crystallize. At a pressure below 3 MPa, liquid He II remains liquid down to the temperature of 0 K. Only under a pressure above 3 MPa can it be solidified at a sufficiently low temperature. Such a behaviour of liquid helium is due to quantum-mechanical effects.

Under high pressures, a decrease in temperature for most of substances also leads to solidification. Exception to this rule is a number of anomalous substances that remain liquid at very high pressures down to the temperature 0 K. Anomalous substances are those whose density decreases during a transition from liquid to solid state, provided that this property is preserved up to very high pressures and low temperatures. The melting point of these substances decreases with increasing pressure. For example, water is an anomalous substance at about 0°C and under nearly atmospheric pressure, since the density of ice is lower than that of water. However, as the pressure increases, ice is converted into other modifications for which anomaly does not exist. Therefore, under very high pressure and at a corresponding temperature water exists in the solid state in the form of ice. Anomalous substances that remain liquids under a sufficiently high pressure down to very low temperatures include, for example, bismuth and antimony.

A transition from liquid to solid state occurs at certain temperature and pressure. This process is called crystallization. The reverse process is called melting (fusion). During melting, heat must be supplied to a substance to convert it from solid to liquid state at a constant temperature. This amount of heat is called the latent heat of fusion. During crystallization, heat of crystallization is liberated. The situation in this case is quite similar to that considered in Sec. 30 in the analysis of phase transition between gaseous and liquid states. Just like the transitions considered there, crystallization and melting are first-order phase transitions.

The latent heat of fusion divided by the mass of a substance is known as the specific latent heat of fusion (Table 6). The specific latent heat of fusion is the amount of heat required to convert 1 kg of a substance from solid to liquid state at the melting temperature, this temperature being constant.

CRYSTALLIZATION AND SUBLIMATION. Under suf-

$$dp = \frac{L}{V_1 - V_2} \frac{dT}{T}$$

Table 6
Melting Point and Specific Latent Heat of Fusion for Some
Substances

Substance	$t_{\text{melt}}, ^\circ\text{C}$	$l, \text{kJ/kg}$
Aluminium	660.1	397.1
Benzene	5.53	128.1
Copper	1083	205
Glycerol	18.4	201.1
Gold	1063	65.7
Hydrogen	-259.2	58.6
Iron (pure)	1535	277.1
Mercury	-38.87	11.8
Silver	960.8	104.5
Water	0.0	333.7
Zinc	419.5	111

ficiently low pressures, a transition to the solid state occurs directly from the gaseous state by-passing the liquid phase, and vice versa, when solid is heated under a certain pressure, it does not melt passing to the liquid state but directly goes over to the gaseous state, or sublimates. Crystallization from the gaseous state and sublimation also occur at a certain temperature and pressure and are accompanied by the absorption or liberation of the latent heat. Consequently, they are also first-order phase transitions.

PHASE DIAGRAMS. The relation between pressure and temperature for a first-order phase transition is given by the Clausius-Clapeyron formula (31.4):

$$\frac{dp}{dT} = \frac{L}{T(V_1 - V_2)}.$$

In the case of liquid-solid and gas-solid transitions, L is the latent heat of crystallization (from the liquid or gaseous state), V_2 is the specific volume of a substance in the solid state, and V_1 is the specific volume of the substance in the liquid state for the liquid-solid transition or in the gaseous state for the gas-solid transition.

For most of substances, the specific volume decreases upon a transition to the solid state, i.e. the density increases. Therefore $V_1 > V_2$ for these substances, and hence $dp/dT > 0$, i.e. the pressure p under which a phase transition occurs increases with temperature.

Thus, the gas-liquid phase diagram (see Fig. 70) can now

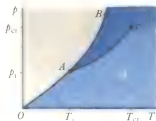


Fig. 122. Gas-liquid-solid phase diagram for a normal substance

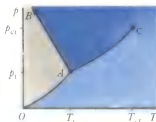


Fig. 123. Gas-liquid-solid phase diagram for an anomalous substance

Crystallization from the gaseous state and sublimation are also first-order phase transitions. They occur at pressure below the triple point.

The density of anomalous substances decreases upon a transition to the solid state. Melting point for such substances decreases with increasing pressure.

be supplemented by liquid-solid and gas-solid phase diagrams. As a result, we get the gas-liquid-solid phase diagram (Fig. 122).

Point A is a triple point: it corresponds to the equilibrium between three phases, viz. gas, liquid, and solid. This is in complete agreement with the phase rule (see Sec. 41). The pressure and temperature corresponding to the triple point are denoted by p_T and T_T . The curve OA is the sublimation curve: under appropriate pressure and temperature, the gas-solid transition occurs without passing through the liquid state. Above the triple point p_T but below the critical pressure p_{cr} , a transition from the gaseous to the solid state may occur only through the liquid phase.

The curve AC corresponds to the liquid-gas transitions. It starts at the triple point A and terminates at the point C denoting the critical state. Above the critical temperature, the difference between the liquid and the gas disappears.

The curve AB characterizes the liquid-solid transition. It does not have a terminal point but continues upwards to infinity (see Fig. 122, arrow in the upper part of the curve). This is due to the fact that the liquid state differs from the crystalline state in structure, and in no case the crystalline structure may become structureless by definition. And it just means that the curve corresponding to the liquid-solid transition does not have a terminal point.

The pressure and temperature corresponding to the triple point for water are respectively equal to $p_T = 6 \text{ Pa}$ and $T_T = 0.01^\circ\text{C}$. Consequently, under normal conditions and atmospheric pressure the sublimation and equilibrium of all phases for water cannot be observed at the triple point. For carbon dioxide, $p_T = 5.16 \times 10^5 \text{ Pa}$ and $T_T = -56.65^\circ\text{C}$, and hence normal conditions are below the pressure corresponding to the triple point. This means that solid carbon dioxide sublimates to the gaseous state under atmospheric pressure, by-passing the liquid phase. This makes it a convenient coolant ("dry ice").

ANOMALOUS SUBSTANCES. For these substances $V_2 > V_1$, and hence $dp/dT < 0$. Their typical phase diagram has the form shown in Fig. 123. The AB curve corresponding to the liquid-solid transition in this case is directed as shown in the figure. This means that the melting point for such materials decreases with increasing pressure, and hence under sufficiently high pressure they can remain liquid down to very low temperatures.

PHASE SURFACES IN THE p, V, T COORDINATES. Each substance in the gaseous, liquid and solid states is characterized by a certain relation between the pressure p ,

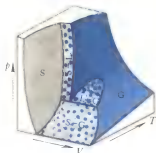


Fig. 124. The typical form of phase surfaces of normal substances in the p, V, T coordinates

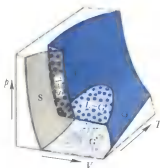


Fig. 125. The typical form of phase surfaces of anomalous substances in the p, V, T coordinates

A second-order phase transition occurs simultaneously in the entire volume which does not change. Latent heat of transition in this case is absent. There is no spatial phase separation and phases do not coexist in equilibrium.

volume V , and temperature T . If we fix one of these parameters, the relation between the other two can be depicted as a curve. This method of analyzing the dependences between the parameters was used for investigating different states of aggregation of a substance. In the general case, the equation of state of a substance has the form

$$\Phi(p, V, T) = 0, \quad (47.1)$$

the function Φ depending on the material and being, generally speaking, a complex function. If we plot along the axes of the three-dimensional Cartesian coordinates the values of p , V , and T , Eq. (47.1) will be depicted by a certain surface in space. Therefore we can say that the equation of state of a substance is represented by a surface in the p, V, T space.

Although the shape of this surface depends on the properties of a specific substance, the general typical features of these surfaces for different classes of materials are the same. Figure 124 shows the typical shape of surfaces for materials whose specific volume decreases upon solidification, while Fig. 125 represents the shape of surfaces for anomalous substances for which the specific volume increases upon solidification. The letters G, L, and S denote the regions of the surfaces corresponding to the gaseous, liquid, and solid state, while the regions S-G, L-G, and S-L of the surfaces correspond to two-phase states solid-gas, liquid-gas, and solid-liquid respectively. The lines on a surface separate the regions corresponding to different phases.

The isotherms, isobars, and isochores are obtained as the points of intersection of the pVT -surface with the planes $T = \text{const}$, $p = \text{const}$, and $V = \text{const}$ respectively. For example, the points of the region L-G (Fig. 124) are depicted by the points on the horizontal lines (see Fig. 66).

Phase diagrams can be obtained by projecting the interfaces onto the coordinate planes. For example, by projecting the interfaces between the phases of the surface (Fig. 124) onto the coordinate plane p, T , we obtain the phase diagram shown in Fig. 122. The line OA in Fig. 122 corresponds to the projection of the S-G surface onto the coordinate plane p, T . The AC line in Fig. 122 is obtained as a result of projecting the L-G surface onto the coordinate plane p, T . Finally, the AB line is the projection of the S-L surface onto the same coordinate plane. Phase diagrams in other variables are obtained similarly.

Thus, the pVT -surfaces contain the most complete information about the states of a substance and about

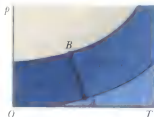


Fig. 126. Phase diagram of helium

Fig. 127. Temperature dependence of the heat capacity in the vicinity of the λ -transition

possible ways of transition from one state to another. However, they are not convenient to use because of purely technical difficulties of constructing three-dimensional surfaces on two-dimensional diagrams. Two-dimensional diagrams, in which the most important dependences for a phenomenon under investigation are retained, are simpler and more convenient to use. This approach was adopted for analyzing most of the problems in this book. In order to employ a pVT -surface directly, it is expedient to construct its three-dimensional model. This is precisely what is done in scientific investigations of states of aggregation of matter.

LIQUID HELIUM. Helium occupies a special place among other substances since it remains in the liquid state under a pressure below 3 MPa at a temperature infinitely close to 0 K. The phase diagram of helium is shown in Fig. 126.

The temperature corresponding to the triple point A lies near 2 K, and the pressure is very low. At a temperature below the triple point, He I does not go over to the solid state as it should be expected. Instead, the phase transition known as the λ -transition takes place. This transition occurs along the AB line. In this transition, helium remains liquid and latent heat is absent. Consequently, it is not a first-order phase transition. It is called λ -transition due to the behaviour of the heat capacity, since the curve describing the heat capacity in the vicinity of the temperature T_λ resemble the Greek letter λ (Fig. 127). At the temperature corresponding to the λ -transition, the heat capacity tends to infinity.

He II is a colourless transparent liquid that does not differ from He I in appearance. The densities of these liquids are equal but they differ significantly in their properties.

When vapour is pumped from the volume occupied by liquid helium, He I intensely boils over the entire volume as the boiling point is attained, while He II does not form bubbles in the liquid, and vaporization of liquid occurs at the interface between the liquid and its vapour. This is a consequence of superthermoconductivity of He II, owing to which the bubbles of superheated vapour are not formed inside the liquid as in an ordinary case.

The most important property of He II is its **superfluidity**, i.e. its ability to flow through narrow holes without friction. Figure 128 schematically illustrates the physical meaning of this phenomenon. For ordinary liquids, the pressure registered by manometer 2 is lower than the one measured by manometer 1 since in the direction of the liquid flow the pressure drops due to friction between the layers of liquid

Fig. 128. Helium II flows through capillaries without friction



$$\rho_c \sim (T_\lambda - T)^{2/3}$$

and between the liquid and the vessel walls. In He II this friction is absent completely, and the readings of the manometers 1 and 2 are identical (provided that the cross-sectional areas of the pipes and the velocity v of the liquid in the regions of measurements are the same).

Such a simple picture of the flow of He II is incomplete and hence not quite correct. Let us move a certain body in He II with a velocity v . Helium II exerts a resistive force F_{fr} on the moving body (Fig. 129), which is in contradiction to the conclusion drawn from the previous experiment about the absence of forces of friction between a moving liquid and the vessel walls. This discrepancy can be explained as follows.

Liquid helium consists of two components, normal and superfluid, which penetrate one another. In a flow through a capillary (see Fig. 128), the normal component is at rest with respect to the vessel walls, while the superfluid component moves without friction relative to the walls and to the normal component. In the second experiment (Fig. 129), the body moves relative to the normal as well as superfluid components. The force of friction directed opposite to the velocity appears due to the motion relative to the normal component. Thus, a two-liquid model of He II completely explains both experiments which at first sight are in contradiction.

The total density of the liquid is equal to the sum of the densities of the normal and superfluid components:

$$\rho = \rho_n + \rho_s. \quad (47.2)$$

The total density is virtually independent of temperature, but its distribution between the normal and superfluid components strongly depends on temperature. As a result, only the superfluid component exists at 0 K and only the normal component at the temperature of the λ -transition.

Superfluidity of He II is manifested only at sufficiently low velocities of flow. There always exists a certain critical velocity of flow above which superfluidity disappears.

The temperature dependence of the ratio of the densities of

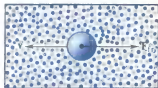


Fig. 129. Helium II exerts resistance to a body moving in it

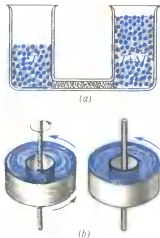


Fig. 130. The fountain effect in Helium (a); superfluid gyroscope (b)

the normal and superfluid components introduces an interesting effect often called the **fountain effect**. Two vessels (Fig. 130a) are connected by a capillary tube filled with a porous material through which the normal component of He II does not penetrate and the superfluid component does. If we raise the temperature in one of the arms, the level of liquid in it will rise. If the vessels are thermally insulated from one another in a proper way, the equilibrium state with different levels of liquid and different temperatures is maintained for a sufficiently long time. A situation resembling osmosis arises, when the pressure of one of the components is balanced through a semipermeable membrane, while the pressure of the component that does not penetrate the membrane is balanced by the membrane itself. It should be noted that the superfluid component ceases to be superthermoconductive if the normal component cannot move.

Another important effect associated with the superfluidity of HeII is the **superfluid gyroscope**. A ring-shaped vessel (Fig. 130b) is filled with liquid HeII and rotated about its axis. Then the rotating fluid is cooled to below the lambda point, as a result of which the vessel becomes filled with HeII rotating with it. After this the rotation is discontinued. However, the superfluid component of HeII continues to move. This motion is manifested as a gyroscopic effect. It is undamped and may last indefinitely long. The angular momentum $L \propto \rho_s \langle v \rangle$, where $\langle v \rangle$ is the average velocity of the superfluid component rotating inside the vessel. Experiments show that L varies with temperature, this dependence being the same as the temperature dependence of ρ_s . This means that it is not the angular momentum of the rotating superfluid component which is conserved but rather its velocity. This cannot be explained simply by the absence of friction.

Helium II is a wetting liquid for all other materials. This is due to the fact that the forces of interaction between helium atoms are weaker than the forces of interaction between helium atoms and any other atoms. For this reason, the level of helium rises near the vessel walls, and helium flows out of the vessel.

The peculiar behaviour of HeII is theoretically explained by considering the condensation of an ideal gas obeying the Bose-Einstein statistics. However, we shall not describe the details of this explanation in this book.

POLYMORPHISM. Solid materials may generally have various crystalline modifications differing in the structure of the crystal lattice. For example, carbon may exist in the form of graphite or in the form of diamond. Several modifications

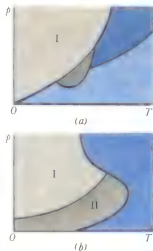


Fig. 131. Phase diagrams for sulphur (a) and carbon (b): I – rhombic modification, II – monoclinic modification

of ice are known to exist. Sulphur has two modifications, and so on. This phenomenon is called polymorphism. A transition of a solid from one crystalline modification to another is called a **polymorphic transformation**. In this case, the crystal lattice undergoes reconstruction.

Each modification exists in a stable form in a certain region of temperature and pressure. The simultaneous existence of two modifications (see Sec. 41) is possible only for a certain relation between the temperature and pressure, i.e. modifications are separated by the lines on the p - T phase diagram.

The phase rule implies that three modifications can be in equilibrium only at a single point (p , T), viz. at the triple point. This means that only three lines separating different modifications can meet at one point on the p - T phase diagram.

Figure 131a shows the phase diagram for sulphur. Sulphur has two modifications in the solid state, viz. monoclinic and rhombic. Figure 131b represents the phase diagram for carbon that has two equally stable modifications: graphite (II) at pressures below 1.5 GPa and diamond (I) at higher pressures. However, diamond may also exist at a not very high pressure. In this case its state is metastable. This is a highly stable state. Diamond can exist in it for a sufficiently long time, and is transformed into graphite only when heated to 1000 K.

Similarly, when the temperature and pressure of graphite are raised to the values corresponding to a stable state for diamond, it remains as graphite and "is in no hurry" to be converted into diamond. Its state is also metastable and is sufficiently stable. Conversion of graphite into diamond required considerable efforts on the part of scientists and engineers and is at present widely used in industry for the production of artificial diamonds.

Polymorphic transformations are phase transitions. They are accompanied by the liberation or absorption of the latent heat of transition, which is associated with a reconstruction of the crystal lattice.

FIRST- AND SECOND-ORDER PHASE TRANSITIONS. The transitions between the liquid and gaseous states (see Sec. 30) were termed **first-order phase transitions**. The liquid-solid transition considered above is also a first-order phase transition.

The equation connecting the pressure and temperature at which a first-order phase transition occurs was derived in Sec. 31.

While considering helium, we came across another type of

phase transition, viz. the lambda transition or the second-order phase transition, as it is more frequently called.

The distinctive feature of first-order phase transitions is an abrupt change in the specific internal energy and related quantities at the transition point, and hence the existence of a latent heat. The transition occurs at a certain temperature and pressure, and the two phases coexist in the volume and are spatially separated during the transition.

Second-order phase transitions occur simultaneously in the entire volume and are always associated with a change in the system symmetry. The temperature at which such a transition occurs is called the Curie point. Since the transition occurs in the entire volume at once, there is no separation of phases in space, and they are not in equilibrium with each other. Therefore, there is no abrupt change in the internal energy, since otherwise the phase transition in the entire volume simultaneously would be simply impossible due to the law of conservation of energy.

This means that a second-order phase transition is not accompanied by a liberation or absorption of the heat of phase transition. In such transitions the volume does not change, but the heat capacity changes due to a change in the system symmetry. This means that the derivative $\partial C_V / \partial T$ changes abruptly, as well as the coefficient of volume expansion $(1/V)(\partial V / \partial T)_p$, although, as was mentioned above, the volume itself is constant.

When we speak about a change in the system symmetry, we do not necessarily mean the crystal symmetry. For example, a transition from the ferromagnetic to the paramagnetic state is not accompanied by a transformation of the crystal structure but is associated with the reorientation of elementary magnetic moments in a body. Transitions of metals to the superconducting state as well as the transition of He I into He II are also second-order phase transitions.

At the present time the theory of second-order phase transitions is being intensely developed. However, there are many questions that require further investigations.

Example 47.1. The molar change in entropy during fusion is known. Find the change in the melting point upon a change Δp in the external pressure. Specific volumes of liquid and solid phases are known, but the specific heat of fusion is not given.

From the Clausius-Clapeyron equation, we find

$$\Delta T = \Delta p T (V_1 - V_2) / L,$$

where L is connected with the change ΔS in entropy through the relation $\Delta S = L/T$ (all quantities correspond to a mole). Then we have

$$\Delta T = \Delta p (V_1 - V_2) / \Delta S.$$

Sec. 48. ALLOYS AND SOLID SOLUTIONS

The definitions of alloys and solid solutions are given. Specific features of crystallization of liquid solutions having a eutectic and noneutectic compositions are compared. Classification of solid solutions is described.

DEFINITION. As a liquid solution is cooled to a certain temperature, crystallization begins. The properties of the solid phase being formed depend on the composition of the solution and may be different. Let us consider two-component substances.

It may happen that a solid phase formed as a result of crystallization consists of a mixture of the crystals of the substance components. Such a phase is called an alloy.

Sometimes, a solid phase formed as a result of crystallization consists of crystals of atoms of both the components. Such a phase is called a solid solution.

ALLOYS. Crystallization in alloys depends on the percentage of the components in a liquid solution. Generally, at a certain temperature the crystallization of one of the components begins. The components crystallize simultaneously only for a quite definite composition of the solution. Such a composition of the liquid solution is called **eutectic**, and the alloy formed as a result of crystallization is called the **eutectic alloy**, or simply **eutectic**.

The phase diagram for such an alloy has the form shown in Fig. 132. The eutectic composition is characterized by the abscissa of the point E. When a liquid solution of such a composition is cooled, the crystals of the two components simultaneously precipitate from the solution at a temperature T_e and the entire process of crystallization is completed at the same temperature. The eutectic alloy formed is a mixture of crystals of the two components. When such an alloy is melted, all the processes occur in the reverse direction.

If the composition of a liquid solution differs from the eutectic, crystallization occurs in a different way. For example if (Fig. 132) a liquid solution is enriched in component B compared to the eutectic composition, and if its composition corresponds to the point C, crystallization starts at a temperature T_1 , but only the crystals of substance B precipitate from the solution. As a result, the liquid solution changes its composition and becomes enriched in substance A. This means that its composition becomes closer to eutectic, and the crystallization temperature decreases.

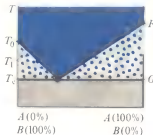


Fig. 132. Constitution diagram of a binary alloy

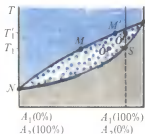


Fig. 133. Constitution diagram of a solid solution

This leads to a change in the crystallization conditions along the CE line. As the point E is reached crystallization occurs at the constant temperature T_e like the crystallization of the eutectic liquid solution. Thus, in liquid solutions having a noneutectic composition, crystallization occurs not at a constant temperature but over a certain temperature interval. The solid phase formed as a result of crystallization consists of large crystals of the component whose content in the solution was higher in comparison with the eutectic composition. The crystals of the other component are smaller and are impregnated between large crystals of the first component. There is no need to repeat this reasoning for the case when the initial solution is enriched in component A instead of component B. In this case the process is similar, the only difference being that the components exchange their roles during crystallization.

Four separate regions are shown in the phase diagram. The T_0EF line separates the liquid state lying above from the two-phase state when both liquid and solid phases are present. There is a region of two-phase states below the T_0E line (liquid solution and solid phase) corresponding to the case when the content of the component B is higher than in the eutectic solution, while the states below the EF line correspond to a predominance of component A in the system. The horizontal line T_eG separates two-phase states from solid states lying below this line.

By way of an example of thoroughly investigated alloys we can consider lead-antimony alloy. The melting points for these metals are 605 and 903 K respectively. The eutectic composition corresponds to 86% lead and 14% antimony, the eutectic melting point being 513 K.

SOLID SOLUTIONS. Solid solutions are divided into substitutional, interstitial, and subtractive. In substitutional solid solutions a part of atoms in the crystal lattice of one of the components is substituted by atoms of the other component. In interstitial solid solutions, atoms of one of the components are implanted between the lattice sites of the other component. Subtractive solid solutions involve the implantation or substitution of atoms of one component by the other component atoms. In addition the lattice of this other component is retained, although with empty lattice sites.

In the simplest case, the phase diagram of solid solutions (Fig. 133) is similar to the phase diagram of liquid solutions (see Fig. 95), the only difference being that the liquid phase (Fig. 133) replaces the gaseous phase (see Fig. 95), while the solid phase (Fig. 133) replaces the liquid phase (see Fig. 95).

All that was said in Sec. 38 in connection with Fig. 95 could be repeated if we replaced a gas by a liquid, a liquid by a solid, and boiling by melting. There is no need to do this here. We recommend the reader to analyze the processes of formation of solid solutions on the phase diagram in Fig. 133 as an exercise.

As in the case of liquid solutions, more complex situations arise for solid solutions like that shown in Fig. 96. Their analysis is rather cumbersome and does not add anything new in principle. Hence, as in the case of liquid solutions, we shall not consider all such possible situations here.

Sec. 49. POLYMERS

General properties of macromolecules and crystalline structures of polymers are described. The shape of macromolecular crystals and their defects are discussed.

INTRODUCTION. In everyday life, solid materials considered in this chapter constitute only a fraction of solid bodies. For example, plant and animal tissues (wood, leather, wool, linen, cotton, etc.), cellulose, glass fibre, rubber, commercial plastics, and many other materials used in everyday life do not belong to the group of solids considered above. These materials also do not include proteins and nucleic acids which play a decisive role in the formation and functioning of living organisms. They constitute a large and important class of substances called **polymers**. For a long time, polymers were and remain a subject of physical chemistry, investigations in this field are carried out mainly by chemists since the basic practical problem is the production of new polymeric materials with required properties, realized by chemical methods. These investigations are continuously broadened, and the role of polymeric materials is becoming more and more important. The number of physicists engaged in polymer studies is continuously on the rise. A large number of monographs are devoted to this subject and polymer physics is becoming a subject not only of chemistry but also physics at the universities. For this reason, some attention will be paid in this book to polymers.

MACROMOLECULES. The molecules of materials conventionally studied in physics consist of a small number of atoms, and their relative molecular mass is usually equal to several tens or at the most a few hundred. For example, a molecule of common salt NaCl consists of only two atoms, and its relative molecular mass is equal to 58. Its crystal lattice with sodium and chlorine atoms at the sites is extremely simple.

However, many molecules have a more complicated composition. The number of atoms constituting a molecule

can be equal to several thousand, and the molecular mass can amount to tens and hundreds of thousands. Such molecules are called macromolecules. The transition from ordinary molecules to macromolecules is continuous, so we must stipulate as to which molecules will be called macromolecules. Usually, it is assumed that a macromolecule must have a relative molecular mass not less than 10 000, and the number of atoms in it must be not less than 1000. Under these conditions, the addition of extra repeating links to a molecule usually does not lead to a considerable change in the physical properties of the material. As an example of one of the simplest protein molecules, we can mention the ribonuclease molecule. It consists of 124 repeating links formed by 17 different aminoacids. Its chemical formula is $C_{575}H_{901}O_{193}N_{171}S_{12}$ and the relative molecular mass is equal to 13 682. A polyethylene molecule whose relative molecular mass is 280 000 has considerably larger dimensions. It consists of 20 000 links of CH_2 groups. **Polymers** are substances formed by macromolecules. They constitute the last class of materials that can be characterized on molecular level. In the limit, a particle of a solid can be formed by one molecule, and the division of the substance into molecules loses its meaning in this case.

The existence of macromolecules was unknown for a long time. Colloids were known to exist long ago. A colloid is an adhesive of gelatin type, having a low diffusion rate and incapable of penetrating through membranes. Other substances, like common salt, have a high diffusion rate in solutions and readily pass through membranes. These substances can be obtained as well-shaped crystals. This explains the term **crystalloids** applied to such materials. It was later found however, that under certain conditions crystalloids can also be transformed into the "colloidal state" if their molecules are made to combine as aggregates. Therefore the colloidal state can be treated as the result of aggregation of molecules with a low relative molecular mass.

Solutions of all substances consisting of macromolecules possess colloidal properties. For this reason it was erroneously considered for a long time that these substances are formed by molecules with a small number of atoms, and the difference between macromolecular colloids and the colloids formed by low-molecular substances was not revealed. This difference was established only in 1920's. The aggregation of crystalloid molecules leading to the appearance of colloidal properties is usually a manifestation

of secondary valency, while the atoms in macromolecules are linked through covalent bonds.

CLASSIFICATION OF MACROMOLECULES. A macromolecule is formed as a result of multiple repetitions of one or several groups of molecules. In the simplest case, these repeating groups form a line. Such macromolecules are called linear. These lines, however, may have diverse shapes, "coiling" of the structure may take place in the motion along this line, and so on. Thus, there is a variety of linear molecules.

However, the macromolecules become even more diverse if we take into account the fact that besides linear macromolecules there also exist branched, ladder, parquet, and three-dimensional molecules. All of them consist of repeating groups of molecules, and their structure is clearly characterized by their names. A repeating group of molecules is called the **monomer**. Usually, a polymer is termed after its monomer with the prefix "poly", like polyethylene. If the repeating links are of the same type, we get **homopolymers**. Different types of links form **copolymers**.

FORMATION OF MACROMOLECULES. There is a large variety of reactions leading to the formation of macromolecules. In the long run, all of them require the conditions under which the appropriate groups of atoms are formed and are eventually linked into a macromolecule. Naturally, this process does not necessarily mean that groups of atoms are formed at first and then connected into a molecule, it is not necessary that the entire molecule be formed simultaneously, etc. For example, when linear high-molecular polymers are formed, the most important reactions are addition polymerization and step polycondensation. In the first case, a molecule as if continuously grows due to the addition of new atoms of the required type in an appropriate sequence. The molecular growth can be terminated as a result of violation of the sequence of addition of atoms: if, for example, an atom of different type occupies a certain position by chance, it can block the entire process of further growth of the molecule.

In the second case, the process as if occurs stepwise. The macromolecule is formed as a result of combination of its parts that can be very large themselves and are formed from smaller fragments as a result of a similar process. The length of a macromolecule formed as a result of such a process is a random quantity. The distribution of molecules with respect to length depends on the equilibrium constant. The shape of molecules, which will be discussed in detail later, is also diverse.

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The number of atoms constituting a macromolecule is several thousand, while the relative molecular mass may be equal to tens and hundreds of thousands. Since a transition from ordinary molecules to macromolecules is continuous, it was assumed that molecules containing more than 1000 atoms and having the relative molecular mass higher than 10 000 are macromolecules.

Macromolecules formed as a result of processes described above differ in size, shape, and other properties. They are incorporated into one class depending on the common monomer forming their basis. However, there is another polymerization process leading to the formation of absolutely identical macromolecules. This process takes place in biosynthesis of macromolecules. The reaction mechanism consists in that monomers are attached to a matrix containing the complete information about the macromolecular structure, thus constituting the appropriate bonds. This leads to the formation of a macromolecule. After this the macromolecule is separated from the matrix, and the matrix is capable of repeating the polymerization cycle. Macromolecules formed as a result of this process are identical since the separation of molecules with lower molecular mass from the matrix, i.e. before the cycle is completed, becomes impossible.

MACROMOLECULAR CONFORMATION. In physics, the shape of macromolecules is called its *conformation*. In the first approximation it is assumed that the shape is the result of a random process of addition of consecutive links. The problem of determining the shape is reduced to the problem of random wandering considered in Sec. 13 in connection with the Brownian movement. The only difference is that in the case of a macromolecule the spacing is constant and equal to the length of the valence bond between consecutive links of the macromolecule. In this approximation, the macromolecule resembles a broken line (see Fig. 22) with all the links of equal lengths. The square of the distance between the start and the end is given by formula (3.3) which in the present case has the form

$$\langle r_n^2 \rangle = a^2 n, \quad (49.1)$$

where $\langle r_n^2 \rangle$ is the mean square distance between the start and the end of a linear macromolecule containing n links and a^2 is the square of the length of the valence bond between consecutive links. Formula (49.1) shows that the linear dimensions of a macromolecule increase in proportion to the square root of the number of links constituting it. Naturally, the random wandering itself occurs in the three-dimensional space.

However, the model of random wandering does not take into account some essential features of the addition of consecutive links in the formation of a macromolecule. First of all, the direction of the bond between atoms is not arbitrary. The direction of a bond is characterized by the valence angle that has practically a definite magnitude.

Consequently, the angles between the directions of consecutive links in the model of random wandering are not arbitrary. Secondly, the rotation about the direction of a bond is hampered, and hence the angle of rotation is also not arbitrary.

These two limitations change formula (49.1). It is clear without calculation that when they are taken into account, the square of the distance between the ends of a macromolecule will increase, i.e. the mean dimension of the macromolecule will be greater.

We must take into consideration one more limitation of the model of random wandering. This model implies that a wandering point may, in principle, return any number of times to the place occupied by it earlier. In the case of a macromolecule, an atom cannot occupy the same place twice. Hence the volumes occupied by the atoms in the process of formation of molecule within the framework of the random wandering model must be excluded from consideration in the following steps. This problem is very complicated from the mathematical point of view. One of the ways of its solution is to reduce all possible conformations to "rotational" isomeric conformations by means of a transition from continuous retarded rotation about the bonds to discrete angles of rotation about these bonds. For example, a polyethylene molecule whose relative molecular mass is 280 000 consists of 20 000 CH_2 groups separated by the valence bonds between them equal in length to 1.54×10^{-10} m. Thus, the total length along the contour of the molecule is 3.08×10^{-6} m. This molecule has three possible rotational isomeric positions of the atoms. In one of the possible cases, the elongated molecule has a plane zigzag conformation with constant valence angles between the bonds. The distance between the ends of such a molecule is equal to 2.53×10^{-6} m. It can be seen that macromolecules are indeed very large and are several times longer than, for example, the wavelength of visible light. Since a polyethylene molecule has three possible isomeric positions of its atoms, and since the number of links in it is 20 000, the total number of rotational isomers for such a molecule is $3^{20\,000}$. This number is extremely large, and hence all possible rotational isomers cannot be realized in a molecule.

There are some other possible ways of isomer formation. For example, the same monomer links can be connected in different ways resulting in different isomeric conformations called **position** or **structural isomers**. Thus, homopolymers have a large variety of isomeric forms. Their number increases even further in the case of copolymers, since in this



A macromolecule is formed as a result of a multiple repetition of one or several groups of molecules called monomers.

Individual macromolecules generally differ from each other in size, shape, and some other properties. They are combined into one class according to monomers on which they are based. Exactly identical macromolecules are formed in the case of a specific mechanism of polymerization, in particular, during biosynthesis of macromolecules.

case the links of several types participate in the creation of isomeric conformations. Isomers have absolutely different properties.

Therefore, a variety of isomeric forms leads to a variety of physical properties of polymers.

CRYSTALLINE STRUCTURE OF POLYMERS. As in the case of ordinary molecules, the system of macromolecules constituting a polymer tends to stable equilibrium corresponding to the minimum of the free energy (see (23.36)).

The minimum free energy is attained for a certain mutual arrangement of atoms constituting the macromolecules. In other words, this requirement determines the shape as well as the mutual arrangement of macromolecules. Naturally, the local conditions ensuring the free energy minimization must be repeated. This means that the polymer structure must be periodic. Thus the crystalline structure of solid polymers is necessitated by the same physical factors as the appearance of the crystal lattice in low-molecular solids.

It follows from theoretical calculations and experimental results that the dependence of the free energy of a polymer on the shape of macromolecules constituting it is much stronger than the dependence on the mutual arrangement of macromolecules. The formation of covalent bonds makes the major contribution to the potential energy of macromolecular crystals. The contribution from the rotation about the bonds (rotational isomerism) is smaller. The smallest contribution is made by the density of packing. For this reason, it is expedient to carry out the analysis of the crystalline structure of polymers in two stages. Firstly, we must analyze the stable conformation of a macromolecule corresponding to the minimum of its free energy, and then consider the mutual arrangement of these molecules. In this case, the same technique is used as in the analysis of crystalline structures formed by ordinary molecules interacting through metallic, ionic, and dispersive forces. It should be recalled that since metallic, ionic, and dispersive forces do not have a definite direction, the calculation of the most stable crystalline structure at a sufficiently low temperature is carried out on the basis of the principle of the most dense packing of interacting particles. The simplest analysis in this case is that of packing identical balls, followed by the analysis of packing two types of balls with different radii, and so on. The conformations of macromolecules whose most dense packing must be investigated are much more diverse and complicated.

One of the possible conformations of a macromolecule is an elongated helix. This conformation can be approximated

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1. What is the structure of linear macromolecules? Which factors determine the diversity of linear macromolecules?
2. Which main types of macromolecules, besides linear, do you know? What are the basic features of their structure?
3. What is the basis of nomenclature of polymers?
4. What do you know about the mechanisms of polymerization and step polycondensation?
5. What is normal crystal structure for a macromolecule (the deviation from which is considered a defect)?
6. What are the sources of defects in macromolecular crystals? Enumerate the most important of them.

by a straight cylinder with circular cross section. The most dense packing of the cylinders corresponds to a spatial structure whose cross section coincides with that for the most dense packing of identical balls. Another frequently encountered macromolecular conformation is a spiral. It can be approximated by a screw with a certain thread. In the analysis of the most dense packing of screws, we must take into account the direction of thread, the nature of entanglement between the screws, and other factors. As a result, we obtain a crystalline structure with a certain symmetry and periodicity. It is important to note that generally the unit cell of a structure is not formed by one macromolecule. Therefore, the size of a unit cell does not coincide with the size of macromolecules, and the same macromolecule extends over many unit cells.

FOLDING OF CHAINS. This is the most important feature of the formation of crystals of linear macromolecules. Only in extremely rare cases the molecules as a result of crystallization have an elongated shape in the crystal. But even in these cases they usually acquire this elongated shape only in the last stage of crystallization. In the initial stage, macromolecular chains are folded. This rule is valid for all flexible linear macromolecules crystallizing from the initially chaotic state. The folding mode and macroconformation of complex chains depend not only on the type of macromolecules but also on the crystallization conditions. For example, macromolecules may crystallize from solutions with different substances as solvents. In this case, the crystallization temperature is different for different solvents. The folding mode considerably depends on the crystallization temperature, pressure, and a number of other similar factors.

Experiments showed that chains mostly fold in such a way that the start and end of a molecular chain are close to one another in the crystal cell. In rare cases the start and end of a molecular chain belong to different crystal cells.

THE SHAPE OF MACROMOLECULAR CRYSTALS. The symmetry of a crystalline structure manifests itself in a regular shape of the crystals and in the symmetry of their faces. This is also valid for macromolecular crystals, although it is much more difficult to grow sufficiently large and perfect crystals of macromolecules in comparison with low-molecular compounds. Here, it is important to determine the behaviour of long macromolecular chains on the surface of crystals. There are many different kinds of the shape of macromolecular crystals and the structure of their surfaces.

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The size of a unit cell does not coincide with the size of a macromolecule. A single macromolecule may pass through many unit cells. However, there are such crystals whose unit cell is formed by one complete macromolecules.

The shape of most of macromolecular crystals is far from perfect. Perfect macromolecular crystals were obtained only in rare cases. Therefore, in most cases polymers are partially crystalline bodies, i.e. they consist of small crystals and amorphous regions.

However, for most of macromolecular crystals their shape is far from perfect. Perfect macromolecular crystals could be obtained only in a comparatively small number of cases. For this reason, polymers are considered to be partially crystalline, i.e. they consist of small crystals and amorphous regions.

DEFECTS OF MACROMOLECULAR CRYSTALS. Since the shape of most macromolecular crystals is far from perfect, we cannot take as a norm an ideal crystalline structure the deviation from which is called a defect. Therefore it is assumed that the norm is a partially crystalline structure characterized by the crystal order parameter. A deviation from the normal value of this parameter characterizes the defects in a crystal. Further, it is assumed that the small crystals contained in partially crystalline structure must be ideal in the norm. Their departure from the ideal shape is a defect in the same sense as in the case of low-molecular crystals. Finally, the third source of defects in a macromolecular crystal is its amorphous part. It is assumed that the structure of an ideal melt is the norm of amorphous parts, and a deviation from this norm is the defect. Taking into account the chain structure of macromolecules, it is assumed that the normal structure of the melt corresponds to a parallel packing of the chains. Sharp bends of chains are treated as defects.

PROBLEMS

- 5.1. Calculate the specific heat capacity of Au, Mg, Na, Cu₂O, and CaO by using the classical law of equipartition of energy. Compare the results with experimental values obtained at 20 °C: 129.6 J/(kg·K), 1.02 kJ/(kg·K), 1.2 kJ/(kg·K), 439 J/(kg·K), and 769 J/(kg·K).
- 5.2. The volume of 1 kmole of iron changes upon melting by $1.03 \times 10^{-3} \text{ m}^3$. Find the change in the melting point of iron upon a change in its pressure by 10^5 Pa .
- 5.3. The entropy of ice changes by 388 J/(K·mole) upon melting. Find the change in the melting point of ice if the external pressure increases by 10^5 Pa .
- 5.4. Find the forces that must be applied to the ends of a steel rod of 1 cm^2 cross section in order to prevent it from elongating upon heating from 0 to 10 °C.
- 5.5. Upon extension of a copper wire with cross-sectional area of 1 mm^2 the residual deformation appears at a load of 29.43 N. Find the elastic limit for copper.
- 5.6. The shear modulus of a material of which a wire is made is 29.43 GPa, its length is 10 cm, and the radius is 0.1 mm. Find the moment of a pair of forces that must be applied to twist the wire by 10° .

- 5.7. Determine the energy spent for twisting a wire 10 cm long and having radius of 1 mm through 10° , if the shear modulus of the material is 100 GPa.
- 5.8. The Poisson ratio for copper is 0.34, and the Young modulus is 2.2×10^{11} Pa. Find the relative change in the density of a cylindrical rod upon its compression under 10^7 Pa.

ANSWERS

5.1. 125 J/(kg·K); 1.02 kJ/(kg·K); 1.08 kJ/(kg·K); 522 J/(kg·K); 890 J/(kg·K). 5.2. $\Delta T = 0.012$ K. 5.3. $\Delta T = 0.009$ K. 5.4. 2.35 kN. 5.5. 29.4 MPa. 5.6. 136 N·m. 5.7. $1.32 \cdot 10^{-13}$ J. 5.8. $\Delta \rho / \rho = 2.8 \cdot 10^{-5}$.



Transport Processes

The driving force of transport processes is the tendency of a system to attain the equilibrium state. *The basic characteristic of the process rate* is the relaxation time.

Sec. 50. THE TYPES OF TRANSPORT PROCESSES

The characteristics of the basic types of transport processes are given and the concept of the relaxation time is introduced.

RELAXATION TIME. Earlier in this book we have considered systems in equilibrium state. If a system is in a nonequilibrium state, it will gradually go over to the equilibrium state if left alone. The time during which the system attains the equilibrium state is called the relaxation time. The relaxation time is different for different parameters in which the system may deviate from the Maxwell equilibrium distribution. The time during which the distribution becomes Maxwellian is called the time of relaxation to the Maxwell distribution, or the thermalization time.

If we have a mixture of two species of molecules whose distribution differs from the Maxwell distribution, both types of molecules will attain the Maxwell velocity distribution after being left alone although in different intervals of time, i.e. their relaxation times are different. If the density distribution over the space for a gas is nonuniform, it will tend to become uniform. The time during which a uniform density is attained is characterized by the relaxation time. Naturally, it is not equal to the time of relaxation to the Maxwell distribution. Thus, a system deviated from the equilibrium position attains equilibrium with different relaxation times for different parameters. It is very important to estimate the relative values of relaxation times, since the processes with the shortest relaxation times bring the system to equilibrium with respect to corresponding parameters very rapidly, and the analysis can be considerably simplified as the system approaches the equilibrium state with respect to the remaining parameters.

THERMAL CONDUCTIVITY. In the equilibrium state, the temperature T is the same at all points of a system. If in a certain region the temperature deviates from the equilibrium value, heat is transported in the system in such a way as to make the temperature of all parts of the system identical. The transfer of heat associated with this transport is called thermal conductivity.

DIFFUSION. In an equilibrium state, the density of each of the components is the same at all points of the phase. If in a certain region the density deviates from the equilibrium value, the motion of the components of the substance occurs in such a way as to make the density of each of the component uniform over the entire volume of the system. The mass transport of the components constituting a phase, associated with this motion, is called diffusion.

VISCOSITY. In the equilibrium state, different parts of a phase are at rest with respect to each other. During their relative motion, factors tending to decrease the relative velocity, i.e. drag forces, or viscosity, come into play. In gases, the mechanism of these forces is reduced to the exchange of the momentum of ordered motion between different gas layers, i.e. to the transfer of the momentum of ordered motion. Hence the drag forces in gases and liquids are also due to a transport process, viz. the transfer of the momentum of the ordered motion of molecules. These three processes will be considered in greater detail in the following sections. In order to be able to analyze these processes quantitatively, we must give quantitative definitions for the basic characteristics of molecular motion.

Sec. 51. KINEMATIC CHARACTERISTICS OF MOLECULAR MOTION

The cross section, collision frequency, and mean free path are considered. The experimental determination of the collision cross section is discussed.

COLLISION CROSS SECTION. A molecule moving in a gas undergoes collisions as a result of which it changes the direction of its motion. Collisions may also have other consequences. For example, a collision may result in ionization. If, for example, we consider the motion of a neutron in the space occupied by uranium nuclei, a collision between the neutron and a uranium nucleus may lead to the capture of the neutron and subsequent fission of the uranium nucleus, accompanied by the liberation of energy. In a concrete situation, all these possible results of collisions can be predicted only with some probability. The probability of a collision leading to a concrete result is described by using the concept of cross section.

An incident particle is assumed to be a point particle, while

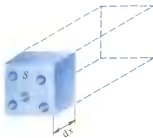


Fig. 134. To the determination of the cross-sectional area

the target particles with which it may collide have such spatial dimensions that the maximum area of their cross section by a plane normal to the direction of motion of the impinging particle is equal to σ . This is an imaginary and not a geometrical area. It is chosen in such a way that the probability of the result of collision under consideration is equal to the probability that the impinging particle, moving in a straight line without interaction, strikes the area σ .

Suppose that an incident particle arrives at the area S of the volume occupied by the target particles with concentration n_0 (Fig. 134). In a layer of thickness dx there are $n_0 S dx$ target particles, and the sum of their cross sections which covers a part of the area S is equal to $dS = \sigma n_0 S dx$. Hence it follows that the probability of the incident particle striking one of the target particles in the layer dx is $d\mathcal{P} = dS/S = \sigma n_0 dx$, (51.1)

where we use the definition (2.3) of the probability.

This is the definition of the cross section σ of the process under consideration. The probability $d\mathcal{P}$ can normally be either calculated by taking into account concrete regularities of the process or measured experimentally, and the cross section is obtained from formula (51.1).

For example, collisions lead to a process in which an incident particle changes the direction of its motion and no longer moves in the given direction. In the case of a neutron moving in a space containing uranium nuclei, the process consists in capturing the neutron by one of the nuclei. In both cases, the quantity being calculated or measured is the probability of the event during the passage of the particle over the distance dx . The quantity calculated by using these data is the cross section σ which, naturally, can be used in further calculations as an initially given quantity.

$$d\mathcal{P} = \sigma n_0 dx$$

MEAN FREE PATH. Obviously, the quantities σ and n_0 do not depend on x . For this reason, the probability of the event increases in proportion to the distance covered by an incident particle. The length of the path $\langle l \rangle$ for which this probability is equal to unity is called the mean free path. In order to determine its value, we obtain from (51.1) the equation $\sigma n_0 \langle l \rangle = 1$, which gives

$$\langle l \rangle = 1/(\sigma n_0). \quad (51.2)$$

This is the distance covered on the average by an incident particle before the collision.

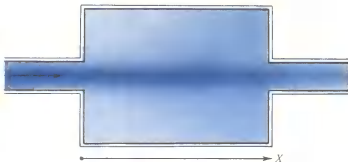


Fig. 135. To the experimental determination of the collision cross section

EXPERIMENTAL DETERMINATION OF THE COLLISION CROSS SECTION. Suppose that an incident beam of particles propagates along the X -axis (Fig. 135). Particles of the beam collide with other particles, change the direction of their motion and escape from the beam. Consequently, the density $I(x)$ of particles in the beam decreases as it propagates through a substance, i.e. with increasing x . Obviously, the decrease dI in the density of the particle flux upon the passage of the layer dx is equal to the number of collisions of particles in the beam with the target particles. Since the probability of collision of each of the particles is given by (51.1), the decrease in the flux density is $I d\mathcal{P}$. Consequently, we obtain the following equation for the density of the particle flux in the incident beam:

$$dI(x) = -I(x) \sigma n_0 dx. \quad (51.3)$$

The minus sign indicates that the density of the particle flux decreases with increasing x , i.e. as the beam propagates through the substance. Solving (51.3), we find

$$I(x) = I(0) \exp(-\sigma n_0 x). \quad (51.4)$$

By measuring somehow the flux density of incident particles at two distances, for example, for $x=0$ and for some other value of x , we can calculate the cross section:

$$\sigma = \frac{1}{n_0 x} \ln \frac{I(0)}{I(x)}. \quad (51.5)$$

The cross sections of other events can be determined experimentally in a similar way. We must only be able to calculate the number of events, measure the flux densities of interacting particles and the paths covered by the particles in the process. Of course, the apparent simplicity of the principle of measurements must not produce an illusion that

$$v' = \sigma n_0 \langle v \rangle$$

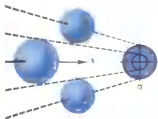


Fig. 136. To the calculation of the collision cross section for rigid spheres

physical measurements are very simple. In actual practice, the measurement of cross sections is an extremely difficult scientific and technical problem.

COLLISION FREQUENCY. An incident particle moves at an average velocity $\langle v \rangle$ and hence covers the mean free path during the time $\tau = \langle l \rangle / \langle v \rangle$. Therefore the average collision frequency (the average number of collisions per second) is equal to

$$\nu' = 1/\tau = \langle v \rangle / \langle l \rangle = \sigma n_0 \langle v \rangle. \quad (51.6)$$

COLLISION CROSS SECTION IN THE RIGID SPHERE MODEL. While considering collisions between identical molecules in gases, the molecules are most frequently treated as rigid spheres of a certain radius r_0 when the cross section and quantities related to it can be easily calculated.

Suppose that target molecules are fixed and an incident molecule moves at a velocity $\langle v \rangle$ (Fig. 136). Obviously, at a distance x the incident molecule will collide with all the target molecules whose centres lie within a circular cylinder with the base of radius $2r_0$ and height x . The mean free path is equal to the height of the cylinder containing one target molecule on the average. Hence we obtain the following equation for determining the mean free path:

$$\pi (2r_0)^2 \langle l \rangle n_0 = 1,$$

from which it follows that

$$\langle l \rangle = 1 / (4\pi r_0^2 n_0). \quad (51.7)$$

According to (51.6) the frequency of collisions between molecules is

$$\nu' = 4\pi r_0^2 n_0 \langle v \rangle. \quad (51.8)$$

Actually, the target molecules move in the gas, and incident molecules have different velocities, the velocities of the target molecules as well as of incident molecules being determined by the Maxwell distribution. In order to take into account these velocities, we may retain the above reasoning, but treat the velocity $\langle v \rangle$ in (51.8) as the average relative velocity of incident molecules. The relative velocity of two molecules moving with velocities v_1 and v_2 respectively is

$$v_{rel} = v_1 - v_2.$$

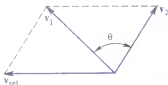


Fig. 137. To the calculation of the mean relative velocity

Hence, we obtain the following expression for the magnitude of the relative velocity:

$$v_{rel} = \sqrt{(v_1 - v_2)^2} = \sqrt{v_2^2 + v_1^2 - 2v_1v_2 \cos \theta}, \quad (51.9)$$

where θ is the angle between the velocity vectors v_1 and v_2 (Fig. 137).

The average value of the relative velocity must be calculated by taking into account the Maxwell distribution (8.16). By directing the Z -axis of the spherical system of coordinates along the vector v_2 , we obtain

$$\begin{aligned} \langle v_{rel} \rangle &= \frac{1}{4\pi} \int_0^{2\pi} d\varphi \int_0^\pi \sin \theta d\theta \int_0^\infty dv_1 dv_2 v_{rel} f(v_1) f(v_2) \\ &= \sqrt{2} \langle v \rangle = \sqrt{16RT/(\pi M)}, \end{aligned} \quad (51.10)$$

where the factor $1/(4\pi)$ takes into account the averaging of the relative velocity over all possible mutual directions of velocities, i.e. over the total solid angle 4π , and $\langle v \rangle$ is the average velocity of molecular motion in the Maxwell distribution, given by formula (8.18).

Thus, taking into account the Maxwell distribution for the velocities of colliding molecules, we obtain the following formulas for the average collision frequency and the mean free path:

$$v' = 4\sqrt{2} \pi r_0^2 n_0 \langle v \rangle = 16r_0^2 n_0 \sqrt{\pi RT/M}, \quad (51.11a)$$

$$\langle l \rangle = 1/(4\sqrt{2} \pi r_0^2 n_0). \quad (51.11b)$$

Under normal conditions in air, $n_0 \approx 10^{25} \text{ m}^{-3}$, $r_0 \approx 10^{-10} \text{ m}$ and $\langle v \rangle \approx 500 \text{ m/s}$, and hence the mean free path and collision frequency are $\langle l \rangle \approx 10^{-8} \text{ m}$ and $v' \approx 10^9 \text{ s}^{-1}$ respectively.

Formula (51.11b) shows that for a fixed temperature, $\langle l \rangle \propto 1/p$, since the pressure is $p = n_0 kT$. This allows us to easily obtain the order-of-magnitude estimates of mean free paths for different pressures. For example, if the air pressure is 133 Pa, the mean free path of molecules is of the order of 10^{-2} cm , while for 1.33 Pa it is of the order of 1 cm.

The collision frequency between the particles contained in 1 m^3 is

$$v_{\text{total}} = n_0 v' / 2 = 8r_0^2 n_0^2 \sqrt{\pi RT/M}.$$

If we have two types of particles with molar masses M_1 and M_2 , we obtain in a similar way the expression for the relative velocity $\langle v_{12} \rangle$:

$$\langle v_{12} \rangle = \left[\frac{8RT}{\pi} \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \right]^{1/2}.$$

The effective radius of collision cross section for molecules having different radii is obviously equal to $(r_{01} + r_{02})/2$, i.e. the half-sum of the effective radii of colliding particles. Denoting by v'_{12} the frequency of collisions between particle 1 and particles 2, we obtain

$$\begin{aligned} v'_{12} &= \pi (r_{01} + r_{02})^2 n_{02} \langle v_{12} \rangle \\ &= 4 \left[\frac{\pi RT}{2} \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \right]^{1/2} (r_{01} + r_{02})^2 n_{02}. \end{aligned} \quad (51.11c)$$

The collision frequency for molecules contained in 1 m^3 is

$$\langle v'_{12 \text{ total}} \rangle = \left[8\pi RT \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \right]^{1/2} (r_{01} + r_{02})^2 n_{01} n_{02}. \quad (51.12)$$

The frequency of collisions between particle 2 and particles 1 is

$$\begin{aligned} v'_{21} &= 4 \left[\frac{\pi RT}{2} \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \right]^{1/2} (r_{01} + r_{02})^2 n_{01} \\ &= (n_{01}/n_{02}) v'_{12}. \end{aligned}$$

THE MEAN FREE PATH OF MOLECULES IN A GIVEN DIRECTION AFTER THE LAST COLLISION. Suppose we have an area element dS (Fig. 138) impinged by molecules coming from all possible directions and crossing it in the direction of negative values of the Z -axis. At what average distance along the Z -axis have the molecules crossing the area element dS at the origin experienced the last collision?

The number of molecules in volume dV is $n_0 dV$. During the time dt , $v' dt$ $n_0 dV$ molecules from the given volume are scattered isotropically as a result of collisions in all possible directions, including the direction towards the area element dS which is seen from the volume element dV at an angle θ . The number of molecules crossing the area element dS , which

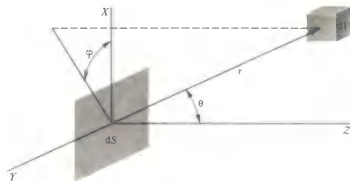


Fig. 138. To the calculation of the mean free path of molecules in a given direction after the last collision

have not experienced a single subsequent collision on their path from the volume element dV is equal to

$$dN = \frac{dS \cos \theta}{4\pi r^2} v' n_0 dV dt \exp(-r/\langle l \rangle), \quad (51.13)$$

where in accordance with formulas (51.4) and (51.2), the factor $\exp(-r/\langle l \rangle)$ takes into account the escape of molecules from the beam due to collisions with other molecules. The flux of particles crossing the surface is given by

$$\begin{aligned} v &= \int \frac{dN}{dS dt} = \frac{v' n_0}{4\pi} \int_0^{2\pi} d\varphi \int_0^{\pi/2} \cos \theta \sin \theta d\theta \int_0^{\infty} dr \exp(-r/\langle l \rangle) \\ &= \frac{1}{4} v' \langle l \rangle n_0 = \frac{1}{4} n_0 \langle v \rangle, \end{aligned} \quad (51.14)$$

where $v' \langle l \rangle = \langle v \rangle$ in accordance with formula (51.6). Formula (51.14) coincides with (8.33).

Let us now calculate the mean distance along the Z -axis, covered by the molecules crossing the area element dS after the last collision. Clearly, this distance is equal to

$$\langle z \rangle = \frac{\int z dN}{\int dN}, \quad (51.15)$$

where dN is given by formula (51.13). Let us calculate (51.15):

$$\langle z \rangle = \frac{1/6 v' n_0 \langle l \rangle^2 dS dt}{1/4 v' n_0 \langle l \rangle dS dt} = \frac{2}{3} \langle l \rangle, \quad (51.16)$$

i.e. the mean distance covered by molecules along the Z -axis after the last collision before crossing the area element dS is not equal to the mean free path but amounts only to $2/3$ of it.

Example 51.1. The effective gaskinetic radius $r_{01} = 1.37 \times 10^{-10}$ m for hydrogen and $r_{02} = 1.87 \times 10^{-10}$ m for nitrogen molecule, while the molar masses of hydrogen and nitrogen are equal to $M_1 = 0.00202$ kg/mole and $M_2 = 0.02802$ kg/mole. The gas mixture occupies the volume 100 l, and the partial pressures of hydrogen and nitrogen are $p_{H_2} = 0.75 p_0$ and $p_{N_2} = 0.25 p_0$ ($p_0 = 0.98 \times 10^5$ Pa). Find the number of collisions between molecules in the vessel during 1 s and the mean free path between collisions for particles of different types.

Taking into account the Dalton law

$$p = (n_{01} + n_{02})kT = n_0 kT,$$

where $n_0 = 2.7 \times 10^{25} \text{ m}^{-3}$ is the Loschmidt number, for the normal conditions we find

$$\begin{aligned} n_{02} &= 0.25n_0 = 0.675 \cdot 10^{25} \text{ m}^{-3}; \quad n_{01} = 0.75n_0 \\ &= 2.025 \cdot 10^{25} \text{ m}^{-3}. \end{aligned}$$

The collision frequency for molecules in 1 m^3 is found with the help of formula (51.12). Then the collision frequency in the entire volume $V = 100 \text{ l}$ is

$$\nu'' = V \langle \nu'_{\text{total}} \rangle = 7.75 \cdot 10^{32} \text{ s}^{-1}.$$

The mean free path for a hydrogen molecule between collisions with nitrogen molecules (see (51.11c)) is

$$\begin{aligned} l_{12} &= \frac{\langle v_1 \rangle}{\nu'_{12}} = \pi^{-1} \left(1 + \frac{M_1}{M_2} \right)^{-1/2} (r_{01} + r_{02})^{-2} n_{02}^{-1} \\ &= 0.43 \cdot 10^{-6} \text{ m}, \end{aligned}$$

where $\langle v_1 \rangle = [8RT/(\pi M_1)]^{1/2}$. Similarly, the mean free path for a nitrogen molecule between collisions with hydrogen molecules is

$$\begin{aligned} l_{21} &= \langle v_2 \rangle / \nu'_{21} = \pi^{-1} (1 + M_2/M_1)^{-1/2} (r_{01} + r_{02})^{-2} n_{01}^{-1} \\ &= 3.9 \cdot 10^{-8} \text{ m}. \end{aligned}$$

Example 51.2. Find the probability that a molecule (atom) of helium covers the distance 0.5 mm without collisions. Helium temperature is 0°C under the pressure 100 Pa. Its gaskinetic radius is 1.9×10^{-10} m.

Using (51.4) and (51.2), we find that the probability of

covering a certain distance without collisions is

$$\mathcal{P}(x) = \exp(-x/\langle l \rangle). \quad (51.17)$$

The mean free path (see (51.11b)) is given by

$$\langle l \rangle = 1/(4\sqrt{2} \cdot \pi r_0^2 n_0) = 0.059 \text{ mm}$$

and hence the required probability is

$$\mathcal{P}(0.5 \cdot 10^{-3} \text{ m}) = \exp(-0.5/0.059) = 2.1 \cdot 10^{-4}.$$

Sec. 52. TRANSPORT PROCESSES IN GASES

The general transport equation is derived and is used for analyzing thermal conductivity, viscosity, and diffusion in gases. Thermal diffusion is considered, and the Gibbs paradox is discussed.

GENERAL TRANSPORT EQUATION. Let G characterize a certain molecular property referred to one molecule. This can be energy, momentum, concentration, or electric charge. In the equilibrium state the quantity G has a uniform value in the entire volume while in the presence of the gradient of G it varies in the direction towards the minimum value.

Let the X -axis be directed along the gradient of G . The mean distance covered by the molecules crossing the area element dS (Fig. 139) after the last collision is, according to (51.16), equal to $2\langle l \rangle/3$. In most cases, this quantity is sufficiently small and the variation of G over the distance $2\langle l \rangle/3$ from the area element dS can be represented in the form

$$G\left(x \pm \frac{2}{3}\langle l \rangle\right) = G(x) \pm \frac{2}{3}\langle l \rangle \frac{\partial G(x)}{\partial x}, \quad (52.1)$$

if we confine ourselves to the first term in the Taylor series expansion at the point x .

The molecular density flux in the direction of the X -axis is equal to $n_0 \langle v \rangle/4$. Consequently, the flux of G through the area element dS towards negative values on the X -axis is

$$I_G^{(-)} = -\frac{1}{4} n_0 \langle v \rangle \left\{ G(x) + \frac{2}{3}\langle l \rangle \frac{\partial G(x)}{\partial x} \right\}, \quad (52.2)$$

the corresponding expression for the flux towards positive values on the X -axis being

$$I_G^{(+)} = \frac{1}{4} n_0 \langle v \rangle \left\{ G(x) - \frac{2}{3}\langle l \rangle \frac{\partial G(x)}{\partial x} \right\}. \quad (52.3)$$

Consequently, the total flux along the X -axis at the point

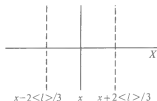


Fig. 139. To the derivation of the general transport equation

x will be

$$I_G = I_G^{(+)} + I_G^{(-)} = -\frac{1}{3} n_0 \langle v \rangle \langle l \rangle \frac{\partial G}{\partial x}. \quad (52.4)$$

This equation is the basic transport equation for the quantity G .

THERMAL CONDUCTIVITY. In this case, G is the mean energy of thermal motion per molecule. This quantity varies with temperature. Here, I_G will be the thermal flux which we denote by I_q . According to the law of equipartition of energy, we have

$$G = \frac{i}{2} kT = \frac{i}{2} \frac{kN_A}{N_A} T = \frac{i}{2} \frac{R}{N_A} T = \frac{C_V}{N_A} T. \quad (52.5)$$

Then the transport equation (52.4) becomes

$$I_q = -\frac{1}{3} n_0 \langle v \rangle \langle l \rangle \frac{C_V}{N_A} \frac{\partial T}{\partial x} = -\lambda \frac{\partial T}{\partial x}, \quad (52.6)$$

where

$$\lambda = \frac{1}{3} n_0 \langle v \rangle \langle l \rangle \frac{C_V}{N_A} = \frac{1}{3} \rho \langle v \rangle \langle l \rangle c_V \quad (52.7)$$

is the thermal conductivity, $\rho = n_0 m$ and $c_V = C_V / (N_A m)$ are the density and specific heat capacity of a gas at constant volume. Equation (52.6) is called the Fourier equation for thermal conductivity, or Fourier's law.

The thermal conductivity doctrine was developed in the second half of the 18th century and was completed in the works by J.B. Fourier (1768-1830) who published his monograph "Théorie analytique de la chaleur" in 1822.

Thermal conductivity can be measured by different methods. Assuming the rigid sphere model for a molecule, we can express $\langle l \rangle$ in formula (52.7) in terms of the radius r_0 of the molecule. The remaining quantities in formula (52.7) can be measured experimentally, while $\langle v \rangle$ for a given temperature is calculated from the Maxwell distribution. Hence this formula can be used for determining the radius of a molecule. The molecular radius calculated in this way is $\sim 10^{-10}$ m, the molecular radius of hydrogen being smaller than the molecular radius of oxygen by a factor of 1.5.

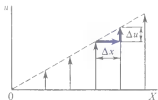


Fig. 140. Mechanism of viscosity

Since the radii of all molecules are approximately the same, the values of C_V for different gases differ only slightly. The main cause of variation of thermal conductivity for a fixed value of concentration n_0 is the difference in the mean velocity $\langle v \rangle$. For this reason, light gases have a considerably higher thermal conductivity than heavy gases. This is confirmed in experiments. Under normal conditions, for example, the thermal conductivity is $0.024 \text{ W/(m}\cdot\text{K)}$ for oxygen and $0.176 \text{ W/(m}\cdot\text{K)}$ for hydrogen. The thermal conductivity of other gases also varies with the mass of their molecules or, which is the same, with their mean velocity $\langle v \rangle$.

Since $n_0 \langle l \rangle = 1/\sigma$ does not depend on pressure, and $\langle v \rangle \propto \sqrt{T}$ is also independent of pressure, we may conclude that the thermal conductivity does not depend on pressure, which is in good agreement with experiments, and increases approximately as the square root of the temperature. We said "approximately" since with increasing temperature the cross section σ slightly decreases. Consequently, the term $n_0 \langle l \rangle$ in (52.7) slightly increases with temperature according to a rather complex law determined by the nature of interaction between molecules. For polyatomic gases, we must also take into account a certain increase in C_V with temperature. The fact that the thermal conductivity does not depend on temperature is confirmed by experimental results.

VISCOSITY. Viscosity, or the internal friction in gases, is caused by the transport of molecular momentum across the direction of motion of the gas layers having different velocities. Figure 140 shows the velocity vectors u of the layers, directed perpendicularly to the X -axis. An arbitrarily chosen layer moves slower than the layer to the right and faster than the layer to the left of it. The division into layers is conventional; Δx is the separation between the layers whose velocities differ by Δu .

As a result of thermal motion, the molecules go over from one layer to another, transferring their momentum from one layer to another. As a result of the exchange of molecules between the layers moving with different velocities, the momentum of the ordered motion of a faster moving layer decreases, while that of a slower moving layer increases. This means that the layer moving faster is decelerated, and that moving slower is accelerated. This is the essence of the mechanism of appearance of the internal friction force between the gas layers moving with different velocities. The force of friction τ divided by the area of friction surfaces is obviously equal to the momentum flux of the ordered motion in a direction perpendicular to the velocity. In the case under consideration,

$$G = \mu u, \quad (52.8)$$

and hence Eq. (52.4) becomes

$$I_{ms} = -\frac{1}{3} n_0 \langle v \rangle \langle l \rangle m \frac{\partial u}{\partial x} = -\eta \frac{\partial u}{\partial x} = \tau, \quad (52.9)$$

where

$$\eta = n_0 \langle v \rangle \langle l \rangle m / 3 = \rho \langle v \rangle \langle l \rangle / 3 \quad (52.10)$$

is the **dynamic viscosity** and $\rho = n_0 m$ is the gas density. The sign of τ indicates that the force of friction acting on faster moving layers is directed against the velocity. Expression (52.10) was obtained for the first time in 1860 by J. Maxwell.

Since $n_0 \langle l \rangle = 1/\sigma$, while $\langle v \rangle \propto \sqrt{T}$, we may conclude that the dynamic viscosity does not depend on pressure and increases almost in proportion to the square root of the temperature (if we ignore the small increase associated with a decrease in the cross section with increasing temperature).

The fact that the dynamic viscosity, i.e. the force of friction, is independent of pressure (and hence of the gas density), is incomprehensible at first sight. This can be explained as follows. The mean free path varies in inverse proportion to pressure, while the molecular concentration is directly proportional to it. The momentum of ordered motion transferred by each molecule is proportional to the mean free path, i.e. is inversely proportional to pressure. Since the concentration of molecules transporting the momentum is directly proportional to pressure, it turns out that the total momentum transferred by molecules, divided by the interval of time and volume, does not depend on pressure. This conclusion is in good agreement with experimental results.

Dynamic viscosity is measured in Pa·s:

$$1 \text{ Pa} \cdot \text{s} = 1 \text{ N} \cdot \text{s} / \text{m}^2 = 1 \text{ kg} / (\text{m} \cdot \text{s}).$$

The dynamic viscosity of gases at 20°C under atmospheric pressure (101.3 kPa) has the order of magnitude of 10^{-5} Pa·s. For example, the viscosities of air, helium, oxygen, and hydrogen are equal to 1.82×10^{-5} , 1.96×10^{-5} , 2.02×10^{-5} , and 0.88×10^{-5} Pa·s respectively.

Along with the dynamic viscosity, the **kinematic viscosity** ν is also used. It is defined as dynamic viscosity per unit

density:

$$\nu = \eta / \rho.$$

Kinematic viscosity is measured in m^2/s .

SELF-DIFFUSION. Suppose that molecules uniformly fill a certain volume. We assume that all the molecules are identical in their mechanical and dynamic parameters, but may differ in a certain property which affects neither the interaction between them nor their motion. Thus, the property being transported in this case is simply the identity of molecules, i.e. the feature of their individual identification. Let us conventionally call this property the "colour" and assume that we have white and black molecules. Suppose that the concentration of white and black molecules in space is not the same. Obviously, in equilibrium the "white" as well as "black" molecules must uniformly fill the entire volume. Therefore, in the case of a nonuniform distribution, the concentrations will level out as a result of collisions between molecules. The transported quantity in this case is the concentration of the molecular species under consideration. Let the concentration of molecules of the first type be $n_1(x)$. Considering that G in Eq. (52.4) is a characteristic of the quantity being transported per molecule, we have

$$G = n_1 / n_0, \quad (52.11)$$

where n_0 is the equilibrium concentration. Equation (52.4) then assumes the form

$$I_{n_1} = -\frac{1}{3} n_0 \langle v \rangle \langle l \rangle \frac{\partial}{\partial x} \left(\frac{n_1}{n_0} \right) = -D \frac{\partial n_1}{\partial x}, \quad (52.12)$$

where

$$D = \langle v \rangle \langle l \rangle / 3 \quad (52.13)$$

is the **diffusion coefficient**. Expression (52.12) is called Fick's law.

For a fixed temperature, $\langle v \rangle$ is constant, while $l \propto 1/p$. Consequently, $D \propto 1/p$ at a fixed temperature. On the other hand, $l \propto T$ and $\langle v \rangle \propto \sqrt{T}$ at a fixed pressure. Consequently, $D \propto T^{3/2}$ at constant pressure. These results were thoroughly verified in experiments. The relation $D \propto 1/p$, which is more conveniently represented as $Dp = \text{const}$, is valid for fairly



In the long run, transport phenomena are due to the tendency of a system to attain the equilibrium state.

A weak dependence of heat capacity of gases on temperature is due to a slight decrease in the collision cross section with increasing temperature.

Dynamic viscosity is independent of the pressure and increases almost in proportion to the square root of the temperature. A small contribution to the temperature dependence of the dynamic viscosity comes from a decrease in the collision cross section with increasing temperature.

rarefied gases over a quite wide interval of pressures to within several tens of percent. The value of D increases with temperature somewhat faster than in proportion to $T^{3/2}$. This can be explained by the fact that with increasing T , the cross section somewhat decreases, which leads to an additional increase in the mean free path.

The diffusion coefficient for atmospheric oxygen and nitrogen under normal conditions has the order of $10^{-5} \text{ m}^2/\text{s}$, as it directly follows from (52.13) if we take into account that $\langle l \rangle \approx 10^{-8} \text{ m}$ and $\langle v \rangle \approx 500 \text{ m/s}$ for these gases.

THE RELATIONSHIP BETWEEN THE COEFFICIENTS CHARACTERIZING THE TRANSPORT EQUATION. It follows from (52.7), (52.10), and (52.13) that

$$\lambda = \eta C_V / (m N_A) = \eta c_V, \quad (52.14)$$

$$D = \eta / \rho = \lambda / (c_V \rho), \quad (52.15)$$

where c_V is the specific heat capacity at constant volume and ρ is the density of a substance. This relationship between the coefficients of transport processes is due to a similar physical nature of transport processes and the fact that they are all described by identical equations of the form (52.4).

MUTUAL DIFFUSION IN A GAS CONSISTING OF DIFFERENT MOLECULES. If there are two types of molecules differing in dynamic properties and in the nature of interaction, the diffusion process becomes much more complicated. For the sake of definiteness, suppose that we have heavy and light molecules. We denote their concentrations by n_1 and n_2 . The condition of constancy of pressure and temperature over the entire volume, following from Dalton's law, has the form

$$n_1 + n_2 = \text{const}, \quad T = \text{const}. \quad (52.16)$$

If n_1 and n_2 separately are not constant over the entire space, the diffusion process must lead to a levelling out of the concentrations. However, the formulas characterizing the diffusion coefficients in this case are not as simple as (52.13).

First of all, it follows from the procedure for deriving (52.4) that this equation is applicable for each of the components of the gas, but the mean free path $\langle l \rangle$ must be calculated by taking into account the collisions not only with the molecules of the same species but also of the other. Consequently, in analogy with (52.12), we can write the following equations for the diffusion fluxes I_{n_1} and I_{n_2} of the molecules of each type:

$$I_{n_1} = -D_1 \partial n_1 / \partial x, \quad I_{n_2} = -D_2 \partial n_2 / \partial x, \quad (52.17)$$

where

$$D_1 = \langle v_1 \rangle \langle l_1 \rangle / 3, \quad D_2 = \langle v_2 \rangle \langle l_2 \rangle / 3, \quad (52.18)$$

and the values of $\langle l_1 \rangle$ and $\langle l_2 \rangle$ are determined by the collisions with both types of molecules.

Obviously, in the general case $D_1 \neq D_2$, and hence the diffusion fluxes I_{n_1} and I_{n_2} do not compensate each other, due to which the constancy of pressure over the entire volume will be violated. Therefore, in addition to the diffusion fluxes, the hydrodynamic flux must appear, i.e. the gas must move as a whole in such a way that the pressure would be maintained constant. Denoting by v the hydrodynamic velocity of the gas flow as a whole, we can write the condition of invariability of pressure in the following form:

$$I_{n_1} + I_{n_2} + (n_1 + n_2)v = 0, \quad (52.19)$$

whence

$$\begin{aligned} v &= -\frac{1}{n_1 + n_2} (I_{n_1} + I_{n_2}) \\ &= -\frac{1}{n_1 + n_2} \left(-D_1 \frac{\partial n_1}{\partial x} - D_2 \frac{\partial n_2}{\partial x} \right) \\ &= \frac{1}{n_1 + n_2} (D_1 - D_2) \frac{\partial n_1}{\partial x}, \end{aligned} \quad (52.20)$$

where we took into account the equality $\partial n_1 / \partial x = -\partial n_2 / \partial x$ obtained by differentiating (52.16). Therefore, the total flux I_1 of the first component, which is the sum of diffusion and hydrodynamic fluxes of this component, is

$$I_1 = I_{n_1} + n_1 v = -\frac{D_1 n_2 + D_2 n_1}{n_1 + n_2} \frac{\partial n_1}{\partial x} = -D_{12} \frac{\partial n_1}{\partial x},$$

(52.21)

where

$$D_{12} = (D_1 n_2 + D_2 n_1) / (n_1 + n_2).$$

(52.22)

Similarly, we obtain the expression for the total flux of the second component:

$$I_2 = I_{n_2} + n_2 v = -D_{21} \frac{\partial n_2}{\partial x},$$

(52.23)

where

$$D_{21} = (D_2 n_1 + D_1 n_2) / (n_2 + n_1) \quad (52.24)$$

is the mutual diffusion coefficient ($D_{12} = D_{21}$).

Thus, the problem involves cumbersome calculations of mean free paths. Maxwell and Stefan proposed the following formulas for calculating these quantities by using the model of rigid and perfectly elastic spheres:

$$\langle l_1 \rangle = \frac{1}{\sqrt{1 + m_1/m_2} 4\pi n_2 R^2}; \quad \langle l_2 \rangle = \frac{1}{\sqrt{1 + m_2/m_1} 4\pi n_1 R^2}, \quad (52.25)$$

where m_1 and m_2 are molecular masses, $R = (r_1 + r_2)/2$, and r_1 and r_2 are the radii of molecules. With the help of these formulas, expression (52.22) can be represented in the form

$$\begin{aligned} D_{12} &= \frac{\sqrt{m_1 \langle v_2 \rangle} + \sqrt{m_2 \langle v_1 \rangle}}{12\pi (n_1 + n_2) R^2 \sqrt{m_1 + m_2}} \\ &= \frac{1}{6\pi (n_1 + n_2) R^2} \sqrt{\frac{2kT}{\pi} \left(\frac{1}{m_1} + \frac{1}{m_2} \right)}, \end{aligned} \quad (52.26)$$

where the velocities $\langle v_1 \rangle$ and $\langle v_2 \rangle$ are replaced by their expressions in terms of the temperature, given by (8.18). Later, a large number of other calculations of the coefficient D were made, in particular, those where the Lenard-Jones potential (29.4) was used. However, the results obtained in this case are very cumbersome and not easy to visualize. They are usually discussed in specialized literature on diffusion. Calculations and measurements show that the coefficient of mutual diffusion of gases is of the order of $10^{-5} \text{ m}^2/\text{s}$ under normal conditions.

THERMAL DIFFUSION. If a temperature gradient is created in a volume V occupied by a gas, the uniform distribution of the gas over the volume is violated. In most cases, the concentration of the light component increases in more heated regions, while the concentration of the heavy component increases in less heated regions, although it is not always the case. This phenomenon is called thermal diffusion.

A steady-state distribution of temperature leads to the establishment of a steady-state distribution of concentrations. However, thermal diffusion takes place in this case. The point

is that the presence of the temperature gradient creates conventional diffusion of molecules, and hence the steady state is ensured by diffusion caused by the temperature gradient (thermal diffusion), that takes place simultaneously in opposite direction.

Thermal diffusion differs in its nature from the transport processes considered above, caused by the collisions between molecules. Thermal diffusion is caused not by the molecular collisions but by the dependence of the frequency of collisions between molecules on their velocity. If the repulsive forces acting between molecules are represented in the form $F \propto 1/r^m$, calculations show that thermal diffusion is absent when $m = 5$. For $m > 5$, thermal diffusion proceeds in such a way that more heated regions are enriched in the lighter component, while for $m < 5$, the heavier component dominates.

The complete theory of diffusion is very complicated. We will limit ourselves to only main points of this problem. In a steady state and for a low temperature gradient, hydrodynamic fluxes are absent, the pressure is constant, and the gas mixture is homogeneous. This means that the following conditions are satisfied:

$$p = nkT = \text{const}, \quad n_1/n = \text{const}, \quad n_2/n = \text{const}, \quad (52.27)$$

where n_1 and n_2 are the concentrations of particles of the gas components, and $n = n_1 + n_2$ is the total concentration of particles in the gas.

Let us direct the X -axis of the coordinate system along the temperature gradient. This allows us to assume that all quantities depend only on the coordinate x . Taking the logarithm of both sides of the first equality in (52.27) and differentiating with respect to x , we find

$$\partial \ln n / \partial x = - \partial \ln T / \partial x. \quad (52.28)$$

On the other hand, it follows from the second and third equalities in (52.27) that

$$\partial \ln n_1 / \partial x = \partial \ln n / \partial x, \quad \partial \ln n_2 / \partial x = \partial \ln n / \partial x. \quad (52.29)$$

A comparison of (52.29) with (52.28) shows that the following relation is valid for each of the components:

$$\frac{\partial \ln n_i}{\partial x} = - \frac{\partial \ln T}{\partial x}. \quad (52.30)$$

Let us now use the Maxwell distribution (8.16). We denote by $N_i(v_i)$ the concentration of i th type molecules whose velocities are close to v_i . Then from (8.16) we obtain

!

In the mutual diffusion in a gas of different molecules, hydrodynamic fluxes existing along with diffusion fluxes play an important role. They appear in order to compensate the nonuniformity of pressure arising from different diffusion rates of the gas components.

Thermal diffusion is caused not by molecular collisions but by the dependence of the collision frequency on the velocity of molecules.

$$N_i(v_i) = dn_i/dv_i = n_i f_i(v_i), \quad (52.31)$$

where n_i is the total concentration of molecules, and $f_i(v_i)$ is given by formula (8.16). In the presence of a temperature gradient, n_i explicitly depends on coordinates, while $f_i(v_i)$ depends on coordinates through the temperature since the temperature gradient is maintained. Then, taking logarithms of both sides of (52.31) and differentiating with respect to x , we obtain

$$\begin{aligned} \frac{\partial \ln N_i(v_i)}{\partial x} &= \frac{\partial \ln n_i}{\partial x} + \frac{\partial \ln f_i(v_i)}{\partial x} = \frac{\partial \ln n_i}{\partial x} + \frac{\partial \ln f_i(v_i)}{\partial T} \frac{\partial T}{\partial x} \\ &= \left(\frac{m_i v_i^2}{2kT} - \frac{5}{2} \right) \frac{\partial \ln T}{\partial x}, \end{aligned} \quad (52.32)$$

where we used (52.30) and took into account the relation $(1/T)(\partial T/\partial x) = \partial \ln T/\partial x$. This means that in the direction of increasing temperature, the concentration of fast molecules, for which $mv^2/(2kT) > 5/2$, increases, while the concentration of slow molecules, for which $mv^2/(2kT) < 5/2$, decreases.

This conclusion is valid for molecules whose velocities are close to v_i . The derivation of formula (52.12) implied that the motion of molecules was traced within the limits of one mean free path. The velocity of a molecule is constant over this distance. Therefore, formula (52.12) can be written for the flux of molecules with the velocity v_i in the form

$$I_{v_i} = -\frac{1}{3} v_i l(v_i) \frac{\partial N_i(v_i)}{\partial x}, \quad (52.33)$$

where $l(v_i)$ is the mean free path for a molecule having the velocity v_i .

This gives the following formula for the total flux of molecules of the i th type:

$$I_i = -\frac{1}{3} \int v_i l(v_i) \frac{\partial N_i(v_i)}{\partial x} dv_i. \quad (52.34)$$

Considering that $\partial N_i(v_i)/\partial x = N_i(v_i) [\partial \ln N_i(v_i)/\partial x]$ and taking into account the equality (52.32), we write the expression for the flux in the form

$$I_i = -\left[\frac{1}{3} \int v_i l(v_i) N_i(v_i) \left(\frac{m_i v_i^2}{2kT} - \frac{5}{2} \right) dv_i \right] \frac{\partial \ln T}{\partial x}. \quad (52.35)$$

Thus, the relation between the direction of the molecular flux and the direction in which the temperature increases depends on the sign of the expression in the brackets. The mean free path $l(v_i)$ is connected with the collision frequency $\nu(v_i)$ through formula (51.6). Taking this formula into consideration, we can write (52.35) as follows:

$$I_t = - \left[\frac{1}{3} \int \frac{v_i^2}{\nu(v_i)} N_i(v_i) \left(\frac{m_i v_i^2}{2kT} - \frac{5}{2} \right) dv_i \right] \frac{\partial \ln T}{\partial x}. \quad (52.36)$$

Obviously, the sign of the integral is determined by the form of the dependence of the collision frequency $\nu(v_i)$ on the velocity of molecules. The integrand changes sign at $m_i v_i^2/2 = 5kT/2$. Therefore, if at low velocities the collision frequency is small and increases sufficiently rapidly with velocity, the integral has a negative value. In this case, the flux is directed towards increasing temperature, and the gas component under consideration is concentrated in the region with higher temperature. On the other hand, if the collision frequency at low velocities is small, and then decreases sufficiently rapidly with increasing velocity, the integral is positive, and the flux is directed against the increasing temperature. Consequently, the given component is concentrated in the less heated region. Obviously, there is an intermediate case when the integral is equal to zero, and hence the flux is absent and no thermal diffusion is observed. This takes place exactly when $m = 5$ in the formula $F \propto 1/r^m$ for the repulsive force.

Thermal diffusion has some important applications, for one, in the isotope separation. Since the masses of isotopes are close, the enrichment of the mixture by one of the component is insignificant for reasonable temperature gradients. For a more complete isotope separation, multistep processes are used and the mixture enriched in the previous stage is used as the initial mixture in the next stage. As a result, the required separation of isotopes can be attained.

GIBBS' PARADOX. According to the second law of thermodynamics, the mutual diffusion of two gases leads to an increase in the entropy of the system. This increase can be calculated by using the method described in Sec. 22 for levelling out pressures and temperatures in a gas.

Initially, the two gases were separated by a partition, and occupied the volumes V_1 and V_2 at the same temperature and pressure. After the partition is removed and diffusion is completed, the gases are mixed and occupy a volume $V_1 + V_2$, the temperature and pressure of the mixture remaining unchanged.

Suppose that we have v_1 moles of the first gas and v_2 moles of the second gas. Then the initially occupied volumes can be found from the condition

$$p_1 = p_2 \quad \text{or} \quad v_1 RT/V_1 = v_2 RT/V_2. \quad (52.37)$$

On the basis of formula (19.6) written for v moles of a gas, the change in the entropy for each of the components in the process of mutual diffusion is

$$\Delta S_1 = v_1 R \ln \frac{V_1 + V_2}{V_1}, \quad \Delta S_2 = v_2 R \ln \frac{V_1 + V_2}{V_2} \quad (52.38)$$

and hence the total change in the entropy of the system is

$$\Delta S = \Delta S_1 + \Delta S_2 = v_1 R \ln \frac{V_1 + V_2}{V_1} + v_2 R \ln \frac{V_1 + V_2}{V_2}. \quad (52.39)$$

The expressions under the logarithms are greater than unity, and hence the entropy of the irreversible process of mutual diffusion increases, as it should be expected.

Suppose now that we have the same gas on both sides of the partition. When the partition is removed, self-diffusion begins. On the one hand, it is clear that the removal of the partition does not in any way affect the state of the gas whose two parts are combined into a single system. Consequently, the entropy must not change after the removal of the partition. But, on the other hand, if we use formula (52.39) for calculating the change in the entropy as a result of self-diffusion, it will turn out that the entropy must increase. This contradictory conclusion is called the Gibbs paradox.

The explanation of the Gibbs paradox involves the elimination of an incorrect physical assumption implicitly used in the reasoning. Considering self-diffusion, we have introduced the concept of the difference between similar molecules, and have thus returned to the concept of different molecules, although this difference can be symbolically expressed by the concept of "colour" of molecules. Hence, let "black" molecules be on one side of the partition and "white" molecules on the other, the molecules being identical in all other respects. Upon mixing of molecules of different colours, the entropy of the system must increase in accordance with formula (52.39), as in the case of mixing of different molecules. However, if all the molecules were of the same colour, the entropy should remain constant upon mixing, since its increase would be in contradiction with its basic property, viz. additivity. Thus, the Gibbs paradox is reduced to the following question: What will happen to the entropy

of the system containing two types of molecules if the black molecules start bleaching and in the long run become white, and as a result the system attains the state with identical molecules? It is clear that bleaching of molecules must not lead to a change in the entropy of the system until the bleached molecules are distinguishable from white ones. However, if we imagine a certain stage of bleaching as a result of which the difference between the bleached and white molecules has vanished, the entropy must change during this period since the number of microscopic states accessible to the system abruptly changes. A continuous transition to identical molecules is impossible without changing the number of microscopic states and entropy. Thus, the Gibbs paradox is eliminated. The molecules may be either identical or different in nature. There is no continuous transition between them. Consequently, the increase in entropy described by formula (52.39) does not contradict the invariability of entropy upon mixing identical molecules.

It was noted by many authors that the Gibbs paradox reflects the relation between macroscopic laws of thermodynamics and the discrete nature of the microworld. Without denying the validity of this remark, we shall consider some other aspects associated with the Gibbs paradox.

It can be easily seen that the transition from the molecules having different colours to the molecules with the same colour must be accompanied by a decrease in the entropy. According to the second law of thermodynamics, this means that this transition cannot occur spontaneously in an isolated system. Consequently, the difference between molecules can be removed only by the action of certain external factors that completely determine the change in the entropy of the system.

Until the difference between the molecules is removed, the entropy of the system decreases to a value corresponding to identical molecules and the Gibbs paradox does not appear.

Example 52.1. Two vessels having the same volume V are connected by a long pipe of length l with a small cross-sectional area S . At the initial moment, the first vessel contains a mixture of gases with concentrations $n_1^{(1)}$ and $n_2^{(1)}$, while the second vessel contains only the gas of the second type with concentration $n_2^{(2)}$. The pressure and temperature are the same in both vessels. Find the change in the concentration $n_1^{(1)}(t)$ of the first gas in the first vessel with time. The diffusion coefficients of the gases are the same and equal to D .

?

1. Which properties associated with molecular motion are transported in the processes of thermal conductivity, diffusion, and viscosity?
2. Why does the collision cross section somewhat decrease with increasing temperature?
3. What is the nature of the hydrodynamic flux appearing in mutual diffusion?
4. Which property of molecular collisions gives rise to thermal diffusion?
5. What is the essence of the Gibbs paradox? Which circumstances must be taken into account in its analysis?

The flux of the first gas to the second vessel is described by the equation

$$I_1 = -D(n_1^{(2)} - n_1^{(1)})S/l, \quad (52.40)$$

where $n_1^{(2)}$ is the concentration of molecules of the first type appearing in the second vessel as a result of diffusion. The condition of conservation of particles of the first type gives

$$Vdn_1^{(1)}/dt = -I_1 = -2DSn_1^{(1)}/l + DS n_{10}/l, \quad (52.41)$$

where $n_{10} = n_1^{(1)}(0)$ and $n_1^{(1)} + n_1^{(2)} = n_1^{(1)}(0) = n_{10}$.

The solution of (52.41) under the initial condition $n_1^{(1)}(0) = n_{10}$ has the form

$$n_1^{(1)}(t) = (n_{10}/2)[1 + \exp(-\alpha t)], \quad \alpha = 2DS/(Vl). \quad (52.42)$$

As $t \rightarrow \infty$, the gas of the first type which initially occupied only the first vessel will be equally distributed between the two vessels. The change in the concentration of the second gas in the first vessel is determined by the requirement that the pressure in the vessel must be constant, i.e. the sum of concentrations of the first and second gases has a constant value. The change in the concentration in the second vessel with time is determined similarly from the conservation condition.

Sec. 53. RELAXATION TIME

Time-dependent transport equations are considered, and the relaxation time for different processes is analyzed. Time-dependent and time-independent problems of thermal conductivity and diffusion are discussed.

FORMULATION OF THE PROBLEM. As a result of transport phenomena, temperatures and concentrations level out, i.e. the temperature and concentration vary with time. If a system is left alone, the temperature and concentration must become the same over the entire gas volume. The time during which this occurs is called the **relaxation time of the system**. To analyze the variation of quantities with time, we need time-dependent equations for thermal conductivity and diffusion.

TIME-DEPENDENT DIFFUSION EQUATION. Let us consider a self-diffusion whose flux is given by Eq. (52.12). We isolate the volume ΔV in the form of a cylinder whose base area is ΔS (Fig. 141) and the height along the X -axis is equal to Δx . According to the definition of the flux, the change in the number of particles in the volume of the cylinder during a time interval Δt is equal to

$$\Delta N_1 = [I_{n_1}(x + \Delta x/2) - I_{n_1}(x - \Delta x/2)] \Delta S \Delta t. \quad (53.1)$$

$$\frac{\partial n}{\partial t} = D \nabla^2 n$$

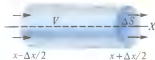


Fig. 141 To the derivation of time-dependent transport equations

Expanding I_{n_1} into a Taylor series and confining ourselves to the term linear in Δx , we obtain

$$I_{n_1}\left(x \pm \frac{\Delta x}{2}\right) = I_{n_1}(x) \pm \frac{\Delta x}{2} \frac{\partial I_{n_1}(x)}{\partial x}. \quad (53.2)$$

Hence, expression (53.1) becomes

$$\Delta N_1 = - \frac{\partial I_{n_1}}{\partial x} \Delta x \Delta S \Delta t. \quad (53.3)$$

Then

$$\lim_{\substack{\Delta V \rightarrow 0 \\ \Delta t \rightarrow 0}} \frac{\Delta N_1}{\Delta V \Delta t} = \frac{\partial n_1}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial n_1}{\partial x} \right), \quad (53.4)$$

where $\Delta V = \Delta S \Delta x$ is the volume under consideration. Since D does not depend on coordinates, we can write instead of (53.4)

$$\frac{\partial n_1}{\partial t} = D \frac{\partial^2 n_1}{\partial x^2}. \quad (53.5)$$

This is the time-dependent self-diffusion equation. If the direction of diffusion does not coincide with the X -axis, but has an arbitrary direction, ΔN_1 in formula (53.1) is represented as the sum of contributions from each of the coordinate axes, and instead of (53.5) we obtain

$$\frac{\partial n_1}{\partial t} = D \left(\frac{\partial^2 n_1}{\partial x^2} + \frac{\partial^2 n_1}{\partial y^2} + \frac{\partial^2 n_1}{\partial z^2} \right) = D \nabla^2 n_1, \quad (53.6)$$

where

$$\nabla^2 = \partial^2 / \partial x^2 + \partial^2 / \partial y^2 + \partial^2 / \partial z^2 \quad (53.7)$$

is the Laplace operator, also denoted by $\Delta = \nabla^2$.

With the help of Eq. (53.6), we can study the change in the concentration n_1 of molecules at all points of the volume if we know the concentration distribution at the initial moment of time (initial conditions) and under certain conditions at the boundary of the volume (boundary conditions). This is a mathematical problem and it is analyzed in detail in mathematical physics.

It should be noted that if mutual diffusion is considered, Eq. (52.2) must be replaced by Eq. (52.21) with the diffusion coefficient D_{12} determined by (52.22). Then, as a result of similar calculations for each of the components, we obtain an equation of the form (53.4) with the diffusion coefficient D_{12} . However, this coefficient depends on coordinates, and we cannot go over to the equation of the type (53.5). In this case, we must solve the system of two nonlinear equations.

TIME-DEPENDENT THERMAL CONDUCTIVITY EQUATION. In this case, the line of reasoning is similar to that in the previous case and the same diagram (Fig. 141) is used, but instead of the particle flux I_{n_i} from (52.12) we must take the heat flux from (52.6). Then instead of (53.4) we obtain

$$\lim_{\substack{\Delta V \rightarrow 0 \\ \Delta t \rightarrow 0}} \frac{\Delta Q}{\Delta V \Delta t} = \lim_{\Delta V \Delta t} \frac{c_V \Delta m \Delta T}{\Delta V \Delta t} = c_V \rho \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left(\lambda \frac{\partial T}{\partial x} \right), \quad (53.8)$$

where $\Delta Q = c_V \Delta m \Delta T$ is the change in the quantity of heat in the volume ΔV during the time Δt , c_V is the specific heat capacity at constant volume, and $\rho = \Delta m / \Delta V$ is the gas density. The thermal conductivity λ is given by formula (52.7). Taking into account (52.15), the equation (53.8) for the thermal conductivity assumes the form identical to Eq. (53.5):

$$\frac{\partial T}{\partial t} = D \frac{\partial^2 T}{\partial x^2} \quad (53.9)$$

with the same diffusion coefficient $D = (1/3) \langle v \rangle \langle l \rangle$. The form of this equation in the case when the heat flux does not coincide with the X -axis is determined in the same way as it was done in connection with Eq. (53.5).

RELAXATION TIME. When a certain quantity deviates from its equilibrium value, there appear the factors tending to return it to this value. The rate at which the equilibrium value is approached is assumed to be proportional to the degree of deviation of the quantity from the equilibrium value. The quantity reciprocal to the proportionality factor is the relaxation time.

Let us consider a quantity q whose equilibrium value is q_0 . Then the above definition can be written in the following form:

$$dq/dt = (q_0 - q)/\tau. \quad (53.10)$$

The solution of this equation has the form

$$(q - q_0) = (q - q_0)_{t=0} e^{-t/\tau}, \quad (53.11)$$

where $(q - q_0)_{t=0}$ is the deviation from the equilibrium value at the initial instant of time $t = 0$. In accordance with the general condition of exponentially varying quantities, τ has the meaning of the time during which the quantity q attains its equilibrium value, i.e. the relaxation time.

RELAXATION TIME FOR CONCENTRATION. Suppose that the concentration or the temperature in a certain volume whose linear dimensions have the order L (the volume is of the order L^3) differ from that of surrounding medium. Then either a heat flux or a particle flux will pass through the surface of this volume in order to equalize the concentration and temperature with their values in the surrounding medium. Let us investigate the law governing the levelling out of these quantities by taking the particle concentration as an example. Clearly, the law of levelling of the temperature will be similar since Eqs. (53.9) and (53.5) are identical.

If $\langle \Delta n \rangle$ is the mean deviation of the particle concentration from the equilibrium value in the volume V , then $V\langle \Delta n \rangle$ is the excess number of particles in the volume in comparison with the number of particles corresponding to the equilibrium density. The particle flux through the surface confining the volume is positive if there is an excess of particles inside the volume, and negative if there is a deficiency of particles. Consequently, the change in the number of particles inside the volume during the time dt is

$$d(V\langle \Delta n \rangle) = -\langle I_n \rangle S dt, \quad (53.12)$$

where S is the area of the surface confining the volume, and $\langle I_n \rangle$ is the mean particle flux through the surface. If the linear dimensions of the volume are L , then $\partial n / \partial x \propto \Delta n / L$, and it follows from Eq. (52.12) that

$$\langle I_n \rangle = D \langle \Delta n \rangle / \langle L \rangle, \quad (53.13)$$

where $\langle L \rangle$ is the mean linear dimension of the volume V , which is determined in such a way that Eq. (53.13) gives the correct value of the average flux $\langle I_n \rangle$ through the surface. The plus sign on the right-hand side of the equation indicates that the flux $\langle I_n \rangle$ must be positive for a positive value of $\langle \Delta n \rangle$. Substituting (53.13) into (53.12), we get

$$d\langle \Delta n \rangle / dt = [-SD / (V\langle L \rangle)] \langle \Delta n \rangle. \quad (53.14)$$



Left alone, a system strives to attain the equilibrium state. The rate of this process is quantitatively characterized by the relaxation time. Relaxation times for different parameters are different.

Time-dependent diffusion and thermal conductivity equations do not take into account the fact that the velocity of propagation of these processes is finite.

The solution of this equation is similar to (53.10) and has the form

$$\langle \Delta n \rangle = (\langle \Delta n \rangle)_0 e^{-t/\tau}, \quad \tau = V \langle L \rangle / (SD), \quad (53.15)$$

where $\langle L \rangle$ does not depend on time. If we take into account the time dependence of $\langle L \rangle$, the solution of Eq. (53.14) assumes the form

$$\langle \Delta n \rangle = (\langle \Delta n \rangle)_0 \exp \left(- \frac{SD}{V} \int_0^t \frac{dt}{\langle L \rangle} \right). \quad (53.16)$$

The quantity

$$\tau_n = V \langle L \rangle / (SD) \quad (53.17)$$

is the time of relaxation to the equilibrium distribution of concentrations. Formula (53.17) makes it possible to analyze the dependence of the relaxation time on different factors. Since $V \propto L^3$, and $S \propto L^2$, we conclude that $\tau \propto L^2/D$. This means that the relaxation time rapidly increases with increasing geometrical dimensions of the region. It is inversely proportional to the diffusion coefficient through which it is related with the gas pressure and temperature.

RELAXATION TIME FOR TEMPERATURE. In this case the calculations are similar, but instead of Eq. (52.13) for the particle flux we must use Eq. (52.6) for the heat flux. As a result, we obtain formula (53.15) in which D must be replaced by the thermal conductivity λ given by (52.7), i.e. put $D = \lambda / (\rho c_V)$. Consequently, the order of the temperature relaxation time is

$$\tau_T = \rho c_V V \langle L \rangle / (\lambda S). \quad (53.18)$$

!

The relaxation time for the concentration rapidly increases with the dimensions of the region and decreases in inverse proportion to the diffusion coefficient.

The temperature relaxation time rapidly increases with the dimensions of the region and decreases in inverse proportion to the thermal conductivity.

TIME-INDEPENDENT AND TIME-DEPENDENT PROBLEMS ON THERMAL CONDUCTIVITY AND DIFFUSION. In order to solve the diffusion equation (53.6) and the corresponding equation for the thermal conductivity, we must set the initial and the boundary conditions. If they are determined and the diffusion coefficient D is known, we have a purely mathematical problem whose solution is considered in detail in appropriate branches of mathematical physics.

Sec. 54. PHYSICAL PHENOMENA IN RAREFIED GASES

Basic features of transport processes in vacuum are analyzed. The exchange of molecules through a porous membrane in rarefied gases and the interaction of molecules with the surface of a solid are considered.

VACUUM. The mean free path increases with decreasing pressure. When it becomes equal to the linear geometrical dimensions of an object, the molecules collide only with the vessel walls (if the volume is confined by the walls) and practically do not collide with each other. Such a situation is called a vacuum. This concept is relative. The larger the linear dimensions of the region, the smaller the pressure at which vacuum is attained. Under normal atmospheric conditions, $\langle l \rangle \sim 10^{-6}$ cm, i.e. the conditions of vacuum are satisfied only for very small volumes with linear dimensions $\sim 10^{-6}$ cm. Since $\langle l \rangle \propto 1/p$, for the pressure $p \approx 10^{-3}$ Pa, $\langle l \rangle \approx 10^2$ cm = 1 m, i.e. the conditions of vacuum are satisfied for sufficiently large volumes.

HEAT TRANSFER UNDER LOW PRESSURE. Since molecular collisions are practically absent in vacuum, the analysis of transport phenomena considered in Sec. 52 is not valid. The molecules move between the walls along the straight lines. Colliding with the walls, they exchange energy with them. Thus, the molecules are the carriers of energy from more heated walls to less heated ones. For this reason, it would be more correct to speak about heat transfer by a gas rather than about its thermal conductivity, since there is no temperature gradient in the volume of the vessel. Rarefied gases have a different pressure dependence of the heat transfer than the pressure dependence for the thermal conductivity at higher pressure. At high pressures, the thermal conductivity is independent of pressure, while the heat transfer at low pressures increases with pressure, since the number of collisions of molecules with the vessel walls increases. Conversely, the heat transfer decreases with pressure to infinitely small values. An example of the practical application of this phenomenon is the Dewar flask. Vacuum created between the flask walls ensures sufficiently small heat transfer.

DIFFUSION AT LOW PRESSURES. Since the collisions between molecules are practically absent, the transport of molecular properties occurs with the velocity of molecular motion, i.e. very rapidly. The time of levelling of the concentration is very small even in very large volumes. This time depends on the shape of the volume.

FRICTION AT LOW PRESSURES. If there are two solid surfaces moving with respect to each other, and if there is a gas at low pressure between them, the forces of friction appearing between the surfaces try to decelerate the faster moving surface and accelerate the slower one. This

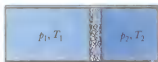


Fig. 142. Equilibrium conditions for gases separated by a porous plug:
 $p_1/\sqrt{T_1} = p_2/\sqrt{T_2}$

phenomenon resembles the appearance of similar forces between moving surfaces under a high air pressure, but the mechanism of this phenomenon is quite different. In vacuum, there are no gas layers moving with respect to each other between friction surfaces. This results in the emergence of forces of internal friction which are transferred from layer to layer. A molecule colliding with the moving surface acquires the corresponding momentum of ordered motion. Having passed the distance separating the surfaces without collision, it exchanges the momentum of its ordered motion with another surface. The momentum transferred to the surface per second is numerically equal to the force of friction. Thus, under vacuum conditions there is no internal friction in the gas in the same sense as under higher pressures, but there is friction between the surfaces moving relative to one another.

VESSELS CONNECTED THROUGH A POROUS PLUG. The pore size in a plug can be so small that the vacuum conditions are satisfied for pores even under normal atmospheric pressure. As a result, a number of interesting phenomena appears.

If the same gas is on both sides of a diaphragm, and different temperatures are maintained, an equilibrium state sets in, in which the pressures on different sides of the partition are different (Fig. 142). Let us denote by subscripts 1 and 2 the quantities corresponding to the different sides of the porous partition. In equilibrium, the number of molecules passing from one half of the volume to the other through the plug is equal to the number of molecules moving in the opposite direction. Since the molecules pass through the pores themselves without collisions, this condition, on the basis of (8.32), can be written as follows:

$$n_{01} \langle v_1 \rangle S_{\text{eff}}/4 = n_{02} \langle v_2 \rangle S_{\text{eff}}/4, \quad (54.1)$$

where S_{eff} is the total effective "area" of pores in the plug.

Considering that $n_0 = p/(kT)$ and $\langle v \rangle = \text{const}/\sqrt{T}$, it follows from (54.1) that

$$p_1/\sqrt{T_1} = p_2/\sqrt{T_2}, \quad (54.2)$$

i. e. the pressure is higher in the part where the temperature is higher. Such a situation would be impossible under normal conditions, since the hydrodynamic flux generated by the difference in pressure would rapidly equalize the pressure. This formula was experimentally verified by Reynolds (1879).

EXCHANGE OF MOLECULES OF DIFFERENT SPECIES THROUGH A POROUS PLUG. Suppose that at a certain moment of time the volumes on the different sides of the

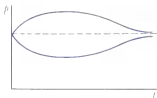


Fig. 143. Time dependence of pressure on different sides of the porous plug for the case of different gases at the same temperature

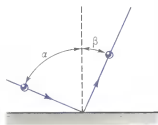


Fig. 144. Reflection of molecules at the surface of a solid

porous plug (Fig. 142) are filled by two different gases at the same temperature and pressure. This is not an equilibrium state. The density of molecules on both sides is the same, but the mean velocities of their motion are different: lighter molecules move faster. Consequently, according to formula (8.32), the frequency of collisions of lighter molecules against the porous plug is higher than for heavier molecules, and hence the number of lighter molecules entering the half of the vessel occupied by heavier molecules per unit time is larger than the number of heavier molecules entering the half occupied by lighter molecules. As a result, the pressure in the part initially occupied by heavier molecules increases, while the pressure in the other part decreases. As the molecules are mixed, the increase in pressure first slows down and then ceases. At this moment, the number of molecules passing through the plug per unit time in both directions becomes the same. However, the concentrations of molecules of each species on different sides of the plug are not equal. The density of molecules in the half containing mostly heavier molecules is higher than in the other half. After this, the number of molecules passing per unit time through the porous plug from the part of the vessel initially occupied by heavier molecules becomes larger than the number of molecules passing through the plug in the opposite direction. The pressure in the first part of the vessel starts to decrease and in the second, increase. Simultaneously with the levelling of the pressure, the concentrations of molecules of each species on both sides of the plug equalize. Figure 143 shows the time dependence of pressure p on different sides of the porous plug in arbitrary units (see Example 54.1).

INTERACTION BETWEEN MOLECULES AND THE SURFACE OF A SOLID. A molecule impinging on a surface interacts only with a small number of atoms and molecules near the surface, exchanges the momentum, and is reflected. In this interaction the angle of incidence is generally not equal to the angle of reflection which depends on specific conditions of interaction between molecules and the surface. Thus, the surface is "coarse". On the average, the angle of reflection β for molecules impinging on the surface in a given direction is smaller than the angle of incidence α (Fig. 144). As a result, in addition to the force of pressure, the surface experiences a tangential force in the direction of the tangential component of the velocity of molecules impinging on the surface. If the molecular fluxes to the surface from different directions are equal, the tangential forces mutually compensate each other, leaving only the pressure on the surface.

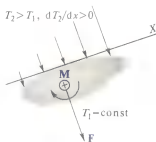


Fig. 145. Emergence of radiometric forces

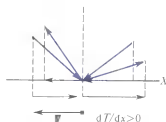


Fig. 146. Emergence of the thermal slip

The energy of molecules reflected at a surface generally changes. If the temperature of the fluxes of molecules impinging on the surface is equal to the temperature of the surface, the temperature of reflected fluxes will be equal to the temperature of incident fluxes. Otherwise, the flux temperature changes as a result of interaction with the surface and becomes equal to the surface temperature.

Let us consider the interaction between molecules and a surface under a high vacuum. In this case, the molecular flux is isotropic and has the same temperature in all directions. If the surface temperature is constant, no tangential forces appear and the pressure is the same at all points of the surface. If, however, the surface temperature changes from point to point, tangential forces are absent as before since the incident molecular flux is isotropic, but the pressure will be different at different points of the surface. In the regions with a higher temperature the pressure is higher, since upon reflection of molecules the normal component of their momentum not only reverses its direction, but also increases in magnitude. As a result, the forces acting on the surface of a body with varying surface temperature in vacuum set its centre of mass in motion and create a moment of rotation about the axis passing through the centre of mass (Fig. 145). These forces are called radiometric.

In the conditions of not very high vacuum the situation is different. The nature of interaction of individual molecules with the surface is the same as in the case considered above (see Fig. 144). However, the surface temperature now affects the gas temperature in a certain layer near the surface, in which collisions between molecules occur. This leads to a change in the properties of the incident molecular flux. If the surface is heated uniformly, then, as before the tangential forces do not appear, while the pressure is the same at all points of the surface. On the other hand, if the temperature at different points of the surface is different, the situation changes. For the sake of definiteness, let the surface temperature increase in the positive direction of the X -axis (Fig. 146). Then the molecules striking a certain region have, on the average, a tangential component, which is larger in the negative direction of the X -axis than in the positive direction, since the first molecules arrive from the side of more heated near-surface layers. Consequently, the resultant of the tangential forces of interaction is directed towards negative values of the X -axis. This force is applied to the surface. According to Newton's third law, the change in the momentum of the molecules having interacted with the surface must be directed oppositely, i.e. towards positive

values of the X -axis. This means that in the surface layer there appears a flux along the surface from less heated regions to more heated regions. This phenomenon is called the **thermal slip**. It follows from what has been said above that it takes place at a not very high vacuum. On the other hand, thermal slip terminates for a certain increase in pressure. The action of forces emerging during thermal slip on the regions of the surface with different temperatures is obvious. They must be added to the forces of pressure shown in Fig. 145.

As the pressure between the regions with different pressures increases, hydrodynamic fluxes appear and equalize the pressure. As a result of an increase in temperature near more heated regions of the surface, the gas pressure in these regions increases and the gas fluxes thus created are directed from more heated regions to less heated regions. These fluxes compensate the thermal slip and equalize the pressure on different regions of the surface. Consequently, radiometric forces, as well as the forces caused by the thermal slip, disappear.

Example 54.1. A vessel is separated into two equal parts by a thin partition with a small hole of area S in it. The volume of the parts are V . Initially, each part of the vessel contains the same number of different molecules at the same temperature. The gases are highly rarefied. The numbers of molecules of types a and b are n_a and n_b ($n_a = n_b$). The mean velocities of molecules at the given temperature are v_a and v_b . The parts of the vessel exchange molecules through the hole. Find the law of time variation of molecular concentrations.

We denote by $n_{a1}(t)$ and $n_{a2}(t)$ the numbers of molecules of type a in the first and the second parts at an instant t . The initial conditions are $n_{a1}(0) = n_a$, $n_{a2}(0) = 0$, $n_{a1} + n_{a2} = n_a = n$. The corresponding conditions for the molecules of type b have the form $n_{b1}(0) = 0$, $n_{b2}(0) = n_b$, $n_{b1} + n_{b2} = n$.

Taking into account (8.33), we may conclude that the number of particles of type a passing per second through the hole S from the first part of the vessel to the second is equal to $(n_{a1}/V) v_a S/4$, and the number of particles passing in the opposite direction is $(n_{a2}/V) v_a S/4$. Consequently, the equation describing the change in the number of molecules in the first part has the form

$$\frac{dn_{a1}}{dt} = -\frac{1}{4} \frac{S v_a}{V} (n_{a1} - n_{a2}) \quad (54.3)$$

! In molecular physics, vacuum is a relative concept and is determined by the relation between the mean free path and the linear dimensions of the vessel containing a gas.

Molecules practically do not interact with each other in vacuum. For this reason, the transport of molecular properties via collisions does not take place in vacuum. Instead, molecular properties are transferred as a result of consecutive collisions of molecules with the surfaces of material bodies.

or, taking into account that $n_{a1} + n_{a2} = n = \text{const}$,

$$\frac{dn_{a1}}{dt} = -\frac{Sv_a}{2V} \left(n_{a1} - \frac{n}{2} \right). \quad (54.4)$$

A similar equation can be written for n_{a2} .

Solving this equation under the initial condition $n_{a1}(0) = n$, we obtain

$$n_{a1}(t) = (n/2) \{1 + \exp[-Sv_a t/(2V)]\}. \quad (54.5)$$

The corresponding expression for $n_{a2}(t)$ is

$$n_{a2} = n - n_{a1} = (n/2) \{1 - \exp[-Sv_a t/(2V)]\}. \quad (54.6)$$

Similar expressions can be obtained for n_{b1} and n_{b2} . The total number of particles in each part varies with time according to the law

$$\begin{aligned} n_1 &= n_{a1} + n_{b1} \\ &= (n/2) \{2 + \exp[-Sv_a t/(2V)] - \exp[-Sv_b t/(2V)]\}, \end{aligned} \quad (54.7)$$

$$\begin{aligned} n_2 &= n_{a2} + n_{b2} \\ &= (n/2) \{2 - \exp[-Sv_a t/(2V)] + \exp[-Sv_b t/(2V)]\}. \end{aligned} \quad (54.8)$$

The pressures in the parts of the vessel are $p_1 = (n_1/V)kT$ and $p_2 = (n_2/V)kT$. Thus, at the initial instant of time the pressures are equal [$p_0 = (n/V)kT$], but then their equality is violated. In the long run, as $t \rightarrow \infty$, the pressures equalize again. The behaviour of the pressures in the process is determined by the mean velocities v_a and v_b : at the initial moment the pressure increases in the part of the vessel containing the gas with a smaller mean velocity of molecules and decreases in the part where this velocity is higher.

SEC. 55. TRANSPORT PHENOMENA IN SOLIDS

The mechanisms of diffusion and thermal conduction in solids are discussed. The meaning of the activation energy of diffusion is clarified. External thermal conductivity is considered.

DIFFUSION. Transport phenomena occur in liquids and solids as well, but the mechanisms of these phenomena differ from those in gases. This is due to the fact that, firstly, the concept of the mean free path loses its meaning here, and secondly, the forces of interaction between the molecules are very large and continuously affect their motion.

Solids exhibit both self-diffusion and mutual diffusion. This is demonstrated in the most visual form by mutual penetration of the substance of two bodies that have been in contact for a sufficiently long time.

Self-diffusion is mainly realized through the following three mechanisms.

1. If there is a vacancy in a crystal lattice site, one of the neighbouring atoms may go over from its site to the vacant site (see Fig. 108). This transition is equivalent to the motion of the vacancy. For the process of self-diffusion to take place due to motion of vacancies, it is necessary that the vacancies be distributed nonuniformly over the lattice, i.e. that the density gradient be created in the lattice. In creating vacancies, a significant role is played by dislocations.

In order to realize diffusion due to motion of vacancies, two conditions must be observed simultaneously: the presence of vacancies and a sufficiently high vibrational energy of neighbouring atoms for one of them to be able to leave its site.

2. If the vibrational energy of an atom in the crystal lattice site has become sufficiently high, the atom can leave its site. If there is no vacancy in the neighbourhood, it becomes an interstitial atom (see Fig. 110) moving in the interstitial space.

3. Neighbouring lattice sites may exchange atoms. This diffusion mechanism is not associated with the motion of lattice defects.

Diffusion in solids is described by Fick's law (52.12), but the diffusion coefficient D is determined by other factors. The motion of vacancies plays a leading role in diffusion. Let us denote by τ the average time of "sedentary" life of the atom at a lattice site and by $\langle d \rangle$ the displacement of the atom during a jump. Obviously, $\langle d \rangle$ is approximately equal to the main lattice period. The mean velocity of atoms during jumps is $\langle v \rangle = \langle d \rangle / \langle \tau \rangle$. Further arguments are similar to those used while deriving Eq. (52.4) and, subsequently, Eq. (52.12). An atom can make a jump by $\langle d \rangle$ in six different directions with equal probability. Consequently,

$$D = \langle v \rangle \langle d \rangle / 6 = (\langle d \rangle)^2 / (6 \langle \tau \rangle). \quad (55.1)$$

In order that a jump be realized, there must be a vacancy and the neighbouring atom must have sufficient energy for accomplishing a jump to the vacancy.

Let us denote by ϵ_v the energy after acquiring which the atom necessarily leaves its site. As a result, a vacancy is formed. In accordance with the Gibbs distribution (7.5), the probability of a vacancy emergence is

$$\mathcal{P}_v = A \exp[-\epsilon_v / (kT)]. \quad (55.2)$$

On the other hand, if we denote by ϵ_j the energy that an atom must have in order to accomplish the jump to the

available vacancy, we can write the following expression for the probability of the jump in the presence of a vacancy:

$$\mathcal{P}_j(\text{jump/vacancy}) = A_j \exp[-\varepsilon_j/(kT)], \quad (55.3)$$

where we use the concept of conditional probability (2.9). Hence the probability that the vacancy exists and the jump to this vacancy is made can be expressed, in accordance with (2.11), as follows:

$$\mathcal{P} = \mathcal{P}_v \mathcal{P}_j = A \exp[-(\varepsilon_v + \varepsilon_j)/(kT)] = A \exp[-W/(kT)], \quad (55.4)$$

where $A = A_v A_j$ is a constant and $W = \varepsilon_v + \varepsilon_j$ is the activation energy of diffusion determined by the properties of the substance.

Obviously, the jump frequency is proportional to the probability of a jump, i.e. $1/\langle\tau\rangle = \mathcal{P}$. Substituting this expression for $\langle\tau\rangle$ into formula (55.1), we find

$$D = D_0 \exp[-W/(kT)], \quad (55.5)$$

where $D_0 = (1/6) \langle d \rangle^2 A$ is a constant defined by the properties of the substance.

The diffusion coefficient for solids is very small (immeasurably smaller than for gases). For example, it is about 10^{-35} m²/s for gold while for atmospheric oxygen it is approximately equal to 10^{-5} m²/s.

THERMAL CONDUCTION. This process is realized through the interaction between molecules rather than through their motion inside a solid. As a result of this interaction, thermal motion acquires a cooperative nature, and hence the thermal motion of molecules in a solid is described as an ideal phonon gas (see Sec. 46).

In order to describe the thermal conductivity, we may repeat the arguments of Sec. 52, bearing in mind that instead of molecular motion we consider the motion of phonons. We obtain the formula similar to (52.6) or heat fluxes, while for the thermal conductivity we can write, in accordance with (52.7), the following expression:

$$\lambda = \rho v_s \langle l_{ph} \rangle c_v / 3, \quad (55.6)$$

where v_s is the velocity of sound in a solid, and $\langle l_{ph} \rangle$ is the mean free path of phonons, whose calculation is difficult

?

1. What is the principal difference between the transport mechanisms in solids and liquids and the transport mechanism for gases?
2. Name three ways of realization of diffusion in solids. What is the order of magnitude of the diffusion coefficient in solids?
3. Which quantities constitute the activation energy of diffusion?
4. How can you explain a very high value of the thermal conductivity of solids in comparison with the thermal conductivity of gases by using the concept of phonons?

problem. This expression shows that $\langle l_{ph} \rangle = \text{const}/T$. The constant is determined by the properties of the material.

Thermal conductivity of solids is many times higher than that of gases. The thermal conductivity of gases under normal conditions has the order of $1 \text{ mW}/(\text{m} \cdot \text{K})$, while for solids it is sometimes of the order of $1 \text{ kW}/(\text{m} \cdot \text{K})$, i.e. 10^5 - 10^6 times higher.

In addition to the lattice conductivity, in metals we must take into account thermal conductivity due to the transport of heat by free electrons. In order to estimate its role, we must take into consideration the properties of the electron gas (see Sec. 27).

At a high temperature, the electron thermal conductivity is significant. It is this component that determines high thermal conductivity of metals in comparison with nonmetals. The lattice thermal conductivity begins to dominate at a lower temperature, while at extremely low temperature, when the lattice thermal conductivity is very small, the electron thermal conductivity predominates again.

EXTERNAL THERMAL CONDUCTIVITY. If a solid is surrounded by a medium with a different temperature, the thermal flux propagates through the surface of the solid. At the surface of the solid, the temperature undergoes a jump from the temperature T of the solid to the temperature T_0 of the medium. Experiments show that for small differences $T - T_0$, the normal component of the heat flux is proportional to this difference:

$$I_{qn} = \alpha (T - T_0), \quad (55.7)$$

where α is the external thermal conductivity. This expression was obtained for the first time in 1701 by I. Newton. The value of the coefficient α is determined experimentally.

Example 55.1. Find the temperature distribution in a spherical layer of a body whose inner surface of a certain radius r_1 is maintained at a temperature T_1 , while the outer surface of radius r_2 , at a temperature T_2 .

The problem is spherically-symmetric, and the thermal flux is directed along the radius. In a steady state, the thermal flux through the spherical surface of any radius between r_1 and r_2 is constant. Consequently, from (52.6) we have

$$\lambda (dT/dr) 4\pi r^2 = \text{const}. \quad (55.8)$$

The general solution of this equation is

$$T = A/r + B, \quad (55.9)$$

where A and B are the integration constants. They are determined by the initial conditions

$$T_1 = A/r_1 + B, \quad T_2 = A/r_2 + B,$$

whence $A = (T_1 - T_2) r_1 r_2 / (r_2 - r_1)$, $B = T_1 - (T_1 - T_2) r_2 / (r_2 - r_1)$, and the solution (55.9) can be written in the form

$$T(r) = (T_1 - T_2) r_1 r_2 / [(r_2 - r_1) r] + (T_2 r_2 - T_1 r_1) / (r_2 - r_1). \quad (55.10)$$

Sec. 56. TRANSPORT PHENOMENA IN LIQUIDS

Specific features of diffusion, thermal conduction, and viscosity in liquids are considered.

DIFFUSION. The mechanism of diffusion in liquids is similar to the diffusion mechanism in solids (see Sec. 55). A molecule changes its surroundings jumpwise and passes to another point. If the mean time of "sedentary" life of a molecule between the jumps is denoted by $\langle \tau \rangle$, we can repeat the arguments of the preceding section and obtain the following expression for the diffusion coefficients instead of (55.1):

$$D = \langle \Delta \rangle^2 / (6 \langle \tau \rangle), \quad (55.1)$$

where $\langle \Delta \rangle$ is the mean distance by which the molecule jumps while changing its surroundings. Recall that in (55.1) $\langle d \rangle$ denotes the mean distance between neighbouring lattice sites.

The time $\langle \tau \rangle$ for liquid is also determined in terms of the probability of a jump. While determining the jump probability, we must take into consideration the required energy and the probability that a molecule has this energy, as well as the probability that there are conditions for a jump in molecular surroundings. Obviously, these two probabilities are given by the formulas of the type (55.2) and (55.3). As a result, we obtain for the diffusion coefficient the formula, which is identical to (55.5):

$$D = D_0 \exp \left[- W / (kT) \right]. \quad (56.2)$$

The activation energy W of a molecule, just as D_0 , is determined by the properties of liquid.

The diffusion coefficient for liquids is much smaller than for gases but much larger than for solids. Its typical order of magnitude is $10^{-9} \text{ m}^2/\text{s}$.

THERMAL CONDUCTION. Thermal conduction in liquids, just as in solids, is realized by the transfer of thermal motion of some molecules to others as a result of interaction.

However, in the case of liquids there is no simple pattern in the form of phonon motion, and the entire theory becomes very complicated and cumbersome if, we try to obtain quantitative results. For this reason, we shall limit ourselves to qualitative remarks and note that the thermal conductivity of liquids is several times higher than that for gases under normal conditions, but it is tens and hundreds of times lower than the thermal conductivity of solids. The only exception is liquid metals whose thermal conductivity is close to that of metallic solids. This is explained by the presence of the electron thermal conductivity in them.

VISCOSITY. The mechanism of viscosity in liquids cannot be represented in a simple form as it was done for rarefied gases in which it is reduced to the transport of the moment of the ordered motion of gas layers upon a transition of molecules from one layer to another as a result of molecular motion. If we adopt this mechanism and take into account the jumpwise transition of a molecule from a "sedentary" state in one layer to a "sedentary" state in another layer, as it was done while deriving (55.5), the temperature dependence of the dynamic viscosity η obtained in this way is in contradiction with the experiment, namely, the theoretical dependence is $\eta \propto \exp(-b/T)$, while the experiments reveal that $\eta \propto \exp(b/T)$.

The mechanism of "jumps" of a molecule from one "sedentary" state to another retained within certain limits, but these jumps must be considered in the direction of action of the force, i.e. perpendicularly to the velocity gradient. In this case, the process turns out to depend on specific features of intermolecular forces. The molecule has to escape from its surroundings in order to move in the direction of the force. The bonds between the molecules that must be overcome in this case are similar to those during evaporation. The calculation of the process is extremely difficult. It reveals that the dynamic viscosity generally depends on the external force, although this dependence is not always significant. In particular, this dependence is unimportant for ordinary liquids at not very high values of the external force.

The dynamic viscosity can be described sufficiently accurately by the formula

$$\eta \approx Ae^{b/T}, \quad (56.3)$$

where A and b are determined by the properties of the liquid. The most important result of this formula is the nature of the temperature dependence of dynamic viscosity: with increasing temperature, the dynamic viscosity abruptly decreases. Such a behaviour of the dynamic viscosity of liquids is opposite to

that observed in gases whose dynamic viscosity increases with temperature.

The dynamic viscosity of conventional, not very viscous liquids is of the order of 1 mPa·s. However, the dynamic viscosity of viscous liquids is thousands of times higher. For example, the dynamic viscosity of water at 20°C is 1.002×10^{-3} Pa·s, 0.648×10^{-3} for petrol, 1.2×10^{-3} for alcohol, and 1480 Pa·s for glycerine. Recall that the viscosity of gases at the same temperature under atmospheric pressure is of the order of 10^{-5} Pa·s.

Sec. 57. BASIC CONCEPTS OF THERMODYNAMICS OF IRREVERSIBLE PROCESSES

The problems of thermodynamics of irreversible processes are considered and its basic concepts are described. The general theory is applied for the analysis of the Seebeck, Peltier, and Thomson effects.

THE OBJECTIVES OF THERMODYNAMICS OF IRREVERSIBLE PROCESSES. The transport processes are irreversible. They have been analyzed on the basis of their mechanisms, but general equations of the form (52.12) for their description are of phenomenological nature. A mechanism of transfer must be considered only for calculating the corresponding transfer coefficient. Thermodynamics of irreversible processes aims at the study of phenomenological laws of irreversible processes, in which the internal mechanisms of these processes are not taken into consideration.

FLUXES AND FORCES. The phenomenological equations describing the transport phenomena discussed above have the form

$$I_q = -\lambda \frac{\partial T}{\partial x}; \quad (57.1)$$

$$I_n = -D \frac{\partial n}{\partial x}; \quad (57.2)$$

$$I_{mu} = -\eta \frac{\partial u}{\partial x}. \quad (57.3)$$

It is expedient to supplement these equations with Ohm's law in the differential form, which will be useful for further applications:

$$j = -\gamma \frac{\partial \phi}{\partial x}, \quad (57.4)$$

where j is the current density, γ the electrical conductivity, ϕ the electric field potential, and $\partial \phi / \partial x$ the electric field

intensity. Thus, Ohm's law (57.4) is also the transport equation for the electric charge.

All these equations are written for one flux component along the X -axis. Similar equations can be written for other two coordinate axes, since fluxes are vector quantities.

The common feature of these equations is that they describe the flux of a certain quantity on the left-hand side of the equation, that appears due to a corresponding driving "force" on the right-hand side of the equation. This force is the gradient of a certain quantity. All the equations for the flux have the form

$$I = LX,$$

where I is the flux of a quantity, X the generalized force creating the flux, and L the proportionality factor.

COUPLED FLUXES. In the cases considered above, each flux was only due to one driving force. However, even the diffusion flux of molecules is caused by two driving forces, viz. the density gradient and the temperature gradient. Therefore, in the general case the expression for the flux I_i has the form

$$I_i = L_{i1} X_1 + L_{i2} X_2 + \dots = \sum_j L_{ij} X_j, \quad (57.5)$$

where the index i labels the type of fluxes, while the index j indicates the type of the driving force. The total number of these equations is equal to the number of fluxes.

Equations (57.5) are called the **linear phenomenological equations of thermodynamics of irreversible processes**, and the coefficients L_{ij} are called the **Onsager coefficients**. The coefficient L_{ii} connects the flux I_i with the corresponding driving force. The coefficients L_{ij} for $i \neq j$ connect different fluxes and forces. They are called the **coupling coefficients**.

ONSAGER RECIPROCAL RELATIONS. It is proved in statistical thermodynamics that the coefficients L_{ij} are not completely independent. The relations

$$L_{ij} = L_{ji}, \quad (57.6)$$

existing between them are called the **Onsager reciprocal relations**. In this book, they are admitted without proof.

GENERATION OF ENTROPY. Another important concept of thermodynamics of nonequilibrium processes is the formula for entropy generation, which will also be given without proof:

$$(dS/dt)_{\text{gen}} = I_1 X_1 + I_2 X_2 + \dots = \sum I_i X_i, \quad (57.7)$$

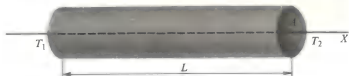


Fig. 147. To the calculation of the entropy generation in a heat flux

where $(dS/dt)_{\text{gen}}$ is the entropy generation rate per unit volume, i.e. the generation rate of the entropy density. Thus, the fluxes I_i and forces X_i cannot be chosen arbitrarily. They must be such that equality (57.7) be observed.

THE CHOICE OF FLUXES AND DRIVING FORCES. While choosing the fluxes and driving forces, we must naturally ensure the same dimensions on both sides of Eq. (57.7), i.e. the following relation between the dimensionalities:

$$\frac{[S]}{[L]^3 [t]} = [I] [X]. \quad (57.8)$$

Here $[L]$, $[t]$, and $[S] = [U]/[T]$ are the dimensions of length, time, and entropy respectively, while $[U]$ and $[T]$ are the dimensions of energy and temperature. Hence we may conclude, for example, that the quantities I_q and $\partial T/\partial x$ in Eq. (57.1) cannot be taken for the flux I_q and the driving force $X_q = -\partial T/\partial x$, since in this case $[I_q][X_q] = [U][T]/([L]^3[t])$, which does not correspond to the dimension of the left-hand side of (57.8). It follows that if we take I_q as a flux we must take $X_q = -(1/T^2)(\partial T/\partial x)$ for the driving force. However, we can naturally take $I = I_q/T$ as a flux, and then we must take $X = -(1/T)(\partial T/\partial x)$ for the driving force.

Similarly, we may conclude that we cannot take the quantity $X = -\partial\phi/\partial x$ for the driving force in Eq. (57.4) if we have the electric charge density $j = I$ as a flux, since $[j][\partial\phi/\partial x] = [U]/[L]^3[t]$. Therefore, the driving force corresponding to the current density j is $X = -(1/T)(\partial\phi/\partial x)$.

GENERATION OF ENTROPY IN THE THERMAL FLUX. On the basis of what has been said above, we may conclude that the entropy in the thermal flux is generated in accordance with the law

$$\left(\frac{dS}{dt}\right)_{\text{gen}} = I_q \left(-\frac{1}{T^2} \frac{\partial T}{\partial x}\right) = -\frac{I_q}{T^2} \frac{\partial T}{\partial x}. \quad (57.9)$$

Let us verify this by direct calculation. We consider a cylinder with a cross-sectional area A and length L (Fig. 147). The lateral surface of the cylinder is insulated, and

its bases are kept at different temperatures T_1 and T_2 , where $T_1 > T_2$.

Under this condition, the flux

$$I_q = -\lambda (\partial T / \partial x) \quad (57.10)$$

or

$$I_q = \lambda (T_1 - T_2) / L \quad (57.11)$$

moves along the cylinder.

The entropy flux is obviously equal to

$$I_S = \frac{I_q}{T} = -\frac{\lambda}{T} \frac{\partial T}{\partial x}. \quad (57.12)$$

Since $\partial T / \partial x = \text{const}$, it is immediately seen from formula (57.12) that the entropy flux density increases along the flow since T decreases. Consequently, the flux generates an entropy during its flow. The entropy generated over a distance dx during 1 s is given by

$$\begin{aligned} \left(\frac{dS}{dt} \right)_{\text{gen}} dx &= A [I_S(x+dx) - I_S(x)] \\ &= AI_q \left[\left(\frac{1}{T} \right)_{x+dx} - \left(\frac{1}{T} \right)_x \right] = AI_q \frac{\partial}{\partial x} \left(\frac{1}{T} \right) dx. \end{aligned} \quad (57.13)$$

Consequently, the generation rate for the entropy density is

$$\left(\frac{dS}{dt} \right)_{\text{gen}} = -\frac{I_q}{T^2} \frac{\partial T}{\partial x}, \quad (57.14)$$

which coincides with (57.9). The entropy generated in the entire volume per second is

$$(\Delta S)_{\text{gen}} = A [I_S(L) - I_S(0)] = AI_q (1/T_2 - 1/T_1). \quad (57.15)$$

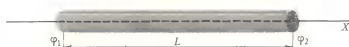
GENERATION OF ENTROPY BY ELECTRIC CURRENT. It follows directly from what has been said above about the form of the driving force for the electric current density that the entropy density generation rate during the passage of electric current is given by

$$\left(\frac{dS}{dt} \right)_{\text{gen}} = -\frac{j}{T} \frac{\partial \phi}{\partial x}. \quad (57.16)$$

Let us verify this by direct calculation. By the Joule law, the current I flowing along a conductor (Fig. 148) produces

$$I_S = -\frac{\lambda}{T} \frac{\partial T}{\partial x}$$

Fig. 148. To the calculation of the entropy generation due to the passage of electric current through a conductor



in it during 1 s the quantity of heat

$$Q = I^2 R = j^2 A^2 L / (A\gamma), \quad (57.17)$$

where $R = L/(A\gamma)$ is the resistance of the conductor. Consequently, the density of the amount of heat liberated per second is

$$\left(\frac{\delta Q}{dV dt} \right)_{\text{gen}} = \frac{Q}{LA} = j^2 / \gamma = -j \frac{\partial \varphi}{\partial x}, \quad (57.18)$$

where we took into account that $j = -\gamma \partial \varphi / \partial x$. Therefore, the entropy generation rate is

$$\left(\frac{dS}{dt} \right)_{\text{gen}} = \frac{1}{T} \left(\frac{\delta Q}{dV dt} \right)_{\text{gen}} = -\frac{j}{T} \frac{\partial \varphi}{\partial x}, \quad (57.19)$$

which coincides with (57.16).

EQUATIONS FOR THERMOELECTRIC PHENOMENA. Let us now consider some more complex phenomena involving coupled fluxes. First of all, let us analyze the densities of the electric current and of the quantity of heat, which are related to one another. In accordance with (57.5), we write the electron and thermal fluxes in the form

$$I_e = -L_{ee} \frac{1}{T^2} \frac{\partial T}{\partial x} - L_{qe} \frac{1}{T} \frac{\partial \varphi}{\partial x}, \quad (57.20)$$

$$j = -L_{eq} \frac{1}{T^2} \frac{\partial T}{\partial x} - L_{ee} \frac{1}{T} \frac{\partial \varphi}{\partial x}. \quad (57.21)$$

For uncoupled fluxes of the thermal and electric conductivities, these equations assume the form

$$I_q = -L_{qq} \frac{1}{T^2} \frac{\partial T}{\partial x}, \quad (57.22)$$

$$j = -L_{ee} \frac{1}{T} \frac{\partial \varphi}{\partial x}. \quad (57.23)$$

Comparing these expressions with (57.1) and (57.4), we see that

$$\lambda = L_{eq}/T^2, \quad (57.24)$$

$$\gamma = L_{ee}/T. \quad (57.25)$$

These expressions can be used for establishing the relation between the quantities L_{eq} and L_{ee} with the thermal conductivity and electric conductivity.

SEEBECK EFFECT. Let us first consider the case when the electric current is absent ($j = 0$). Equation (57.21) then becomes

$$0 = -L_{eq} \frac{1}{T^2} \left(\frac{\partial T}{\partial x} \right)_{j=0} - L_{ee} \frac{1}{T} \left(\frac{\partial \varphi}{\partial T} \right)_{j=0}, \quad (57.26)$$

whence

$$\frac{(\partial \varphi / \partial x)_{j=0}}{(\partial T / \partial x)_{j=0}} = - \frac{L_{eq}}{L_{ee} T}. \quad (57.27)$$

Taking into account the relation

$$\frac{(\partial \varphi / \partial x)_{j=0}}{(\partial T / \partial x)_{j=0}} = \left(\frac{\partial \varphi / \partial x}{\partial T / \partial x} \right)_{j=0} = \left(\frac{\partial \varphi}{\partial T} \right)_{j=0}, \quad (57.28)$$

we can write Eq. (57.27) in the form

$$(\partial \varphi / \partial T)_{j=0} = -L_{eq} / (L_{ee} T). \quad (57.29)$$

This means that in the absence of electric current but in the presence of a temperature gradient, a potential difference appears. In other words, the temperature gradient generates electric current. This effect is called the Seebeck effect. The quantity

$$E_T = -(\partial \varphi / \partial T)_{j=0} = L_{eq} / (L_{ee} T) \quad (57.30)$$

is called the thermoelectromotive force.

COUPLED ELECTRIC CURRENT AND HEAT FLUX. Expressing $\partial \varphi / \partial x$ for $j = 0$ in terms of $\partial T / \partial x$ in accordance with (57.21) and substituting the result into (57.20), we find

$$I_{||} = -L_{qq} \frac{1}{T^2} \frac{\partial T}{\partial x} + \frac{L_{eq}^2}{L_{ee}} \frac{1}{T^2} \frac{\partial T}{\partial x} = \frac{-L_{qq} L_{ee} + L_{eq}^2}{T^2 L_{ee}} \frac{\partial T}{\partial x}, \quad (57.31)$$

where $L_{eq} = L_{qe}$. The quantity

$$\lambda_T = (L_{qq} L_{ee} - L_{eq}^2) / (T^2 L_{ee}) \quad (57.32)$$

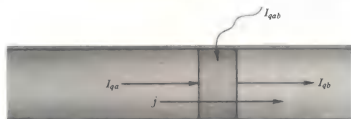


Fig. 149. To the explanation of the Peltier effect

is the thermal conductivity in the system of coupled electric current and heat flux.

It follows from (57.30) that

$$L_{eq} = E_T T L_{ee} = E_T T^2 \gamma, \quad (57.33)$$

where we took into account (57.25). Using (57.24), (57.32), and (57.33), we can give Eqs. (57.20) and (57.21) the following form:

$$I_q = -(\lambda_T + E_T^2 \gamma T) \frac{\partial T}{\partial x} - E_T T \gamma \frac{\partial \phi}{\partial x}, \quad (57.34)$$

$$j = -E_T \gamma \frac{\partial T}{\partial x} - \gamma \frac{\partial \phi}{\partial x}. \quad (57.35)$$

PELTIER EFFECT. Eliminating from (57.34) $\partial \phi / \partial x$ with the help of (57.35), we obtain the expression for the heat flux:

$$I_q = -\lambda_T \frac{\partial T}{\partial x} + E_T T j. \quad (57.36)$$

Let us now consider the conditions at the junction between two different conductors (Fig. 149) under isothermal conditions.

If the conductors are at the same temperature, i.e. $\partial T / \partial x = 0$, the current with the density $j = -\gamma \partial \phi / \partial x$ passes through the junction. Heat fluxes on different sides of the junction are different in this case. According to (57.36), they are equal to

$$I_{qa} = E_{Ta} T j, \quad (57.37)$$

$$I_{qb} = E_{Tb} T j. \quad (57.38)$$

Since the quantities of heat supplied to the junction and leaving it are different, the heat is either absorbed or

$$I_{qab} = A\pi_{ab}j$$

liberated at the junction. Thus, upon a passage of electric current through the junction between two different metals, the junction is either heated or cooled. This phenomenon is called the Peltier effect. Under isothermal conditions, the temperature of the junction is maintained constant due to heat exchange with the ambient.

The thermal power liberated or absorbed at the junction is

$$I_{qab} = A(I_{qb} - I_{qa}) = AT(E_{Tb} - E_{Ta})j = A\pi_{ab}j, \quad (57.39a)$$

where

$$\pi_{ab} = T(E_{Tb} - E_{Ta}) \quad (57.39b)$$

is the Peltier coefficient.

THOMSON EFFECT. Let us maintain a temperature gradient along a current-carrying conductor (Fig. 150). The energy flux I_E along the conductor is the sum of the heat flux I_q (see (57.36)) and the energy flux ϕj associated with the motion of electric charges. Consequently, the total energy flux is

$$I_E = I_q + \phi j = -\lambda_T \partial T / \partial x + (E_T T + \phi) j. \quad (57.40)$$

Let us consider a cylindrical layer of thickness dx in the conductor (Fig. 150). The energy liberated in this layer appears due to the difference in the energy fluxes through the surface confining this layer. Consequently, the energy liberated in the layer per second is

$$\frac{dQ}{dt} = A [I_E(x + dx) - I_E(x)] = A \frac{\partial I_E}{\partial x} dx, \quad (57.41)$$

where A is the cross-sectional area of the conductor. Substituting the expression (57.40) for I_E into this equation, we finally obtain the following expression for the thermal power density liberated in the conductor upon the passage of the current through it:

$$\tau = T \frac{DE_T}{\partial T}$$

$$\mathcal{P}_V = \frac{dQ}{A dx dt} = -\frac{\partial}{\partial x} \left(\lambda_T \frac{\partial T}{\partial x} \right) + Tj \frac{\partial E_T}{\partial x} - \frac{j^2}{\gamma}, \quad (57.42)$$

where $\partial \phi / \partial x = -j/\gamma$.

The last term on the right-hand side of this equation describes the quantity of heat liberated in a conductor upon the passage of the current in accordance with Joule's law.

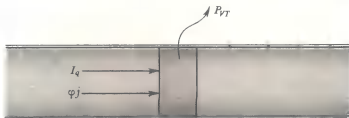


Fig. 150. To the explanation of the Thomson effect

According to the rule of signs (see Sec. 14), the minus sign indicates that the heat is liberated in the system. The first term describes the heat flow independent of the electric current. The presence of the middle term shows that due to the temperature gradient, a heat is liberated or absorbed in a conductor in addition to the Joule heat. This additional heat is called the Thomson heat. According to (57.40), the density of the Thomson heat power is equal to

$$P_{VT} = Tj \frac{\partial E_T}{\partial x} = Tj \frac{\partial E_T}{\partial T} \frac{\partial T}{\partial x} = \tau j \frac{\partial T}{\partial x}, \quad (57.43)$$

where

$$\tau = T \frac{\partial E_T}{\partial T} \quad (57.44)$$

is the Thomson coefficient.

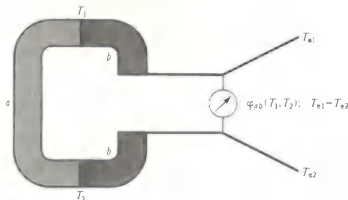
Liberation or absorption of heat in addition to Joule's heat, which takes place in a current-carrying conductor with a temperature gradient, is called the Thomson effect.

THERMOCOUPLE. Let us consider an open circuit consisting of two different conductors the junctions between which are kept at different temperatures T_1 and T_2 (Fig. 151). The same temperature gradient in the conductors produces Seebeck effects of different magnitudes in them. In other words, the potential difference is created. A combination of two Seebeck effects in different conductors creates an electromotive force in the circuit.

In accordance with (57.30), the potential difference φ_{ab} is given by

$$-\varphi_{ab} = \int_{T_{c1}}^{T_1} E_{Tb} dT + \int_{T_1}^{T_2} E_{Ta} dT + \int_{T_2}^{T_{c2}} E_{Tb} dT, \quad (57.45)$$

$$\mathcal{P}_{VT} = \tau j \frac{\partial T}{\partial x}$$

Fig. 151. Thermocouple ($T_1 > T_2$)

where T_{e1} and T_{e2} are the temperatures of the ends of the conductors between which the potential difference φ_{ab} is measured. For $T_{e1} = T_{e2}$ formula (57.45) assumes the form

$$-\varphi_{ab} = \int_{T_1}^{T_2} [E_{Ta} - E_{Tb}] dT. \quad (57.46)$$

For $T_2 - T_1 \rightarrow 0$ K, we have

$$d\varphi_{ab}/dT = E_{Tb} - E_{Ta} = \alpha_{ab}(T), \quad (57.47)$$

where $\alpha_{ab}(T)$ is the **Seebeck coefficient**. Using (57.39b), we can express $\alpha_{ab}(T)$ in terms of the Peltier coefficient π_{ab} :

$$\alpha_{ab} = \pi_{ab}/T. \quad (57.48)$$

Formula (57.46) establishes a one-to-one correspondence between the temperatures T_1 , T_2 and the potential difference φ_{ab} . Therefore, if we take the known temperature T_2 as the reference point, we can reduce the measurement of other temperatures to the measurement of the potential difference. This makes thermocouples very convenient instruments for measuring temperature.

PROBLEMS

- 6.1. A one-component gas with the relative molecular mass $M_r = 29$ has the pressure $p = 10^5$ Pa and temperature $T = 273$ K. Find the collision frequency in a volume of 1 l, the collision frequency for an individual particle, and the mean free path, assuming that the gaskinetic radius of the gas molecules is $r_0 = 1.87 \times 10^{-10}$ m.
- 6.2. The gaskinetic radius of helium atoms can be assumed equal to $r_0 = 1.09 \times 10^{-10}$ m. Find the total number of particles in 1 m³,

which during 1 s may cover the distance 0.5 cm without collisions. The pressure is 100 Pa, the temperature 0°C.

- 6.3 Find the probability that a particle passes without collisions a distance equal to two-, three-, and fivefold mean free path.
- 6.4 Find the pressure under which the mean free path of hydrogen molecules at 0°C is equal to 1 cm.
- 6.5 Assuming that the gaskinetic radii of H_2 and CO_2 molecules are equal to $r_{01} = 1.35 \times 10^{-10}$ m and $r_{02} = 2.3 \times 10^{-10}$ m respectively, while their partial pressures are $p_1 = 1.96 \times 10^5$ Pa and $p_2 = 0.98 \times 10^5$ Pa, find the mean free paths between collisions of molecules of different species. The temperature is 0°C.
- 6.6 The dynamic viscosity of hydrogen is $\eta = 8.6 \times 10^{-6}$ Pa·s at $T = 273$ K and $p = 1.01 \times 10^5$ Pa. Find the mean free path of hydrogen molecules and the gaskinetic radius.
- 6.7 Find the dynamic viscosity of nitrogen under normal conditions if its diffusion coefficient is 1.42 m²/s.
- 6.8 Find the gaskinetic radius of oxygen molecules if its dynamic viscosity at 0°C is 18.8×10^{-6} Pa·s.
- 6.9 Assuming that the gaskinetic radius of a gas molecule is 1.5×10^{-10} m, find the diffusion coefficient and the dynamic viscosity of the gas at $p = 1.01 \times 10^5$ Pa and $T = 283$ K.
- 6.10 Find the thermal conductivity of a gas the gaskinetic radius of whose molecules is 1.5×10^{-10} m, temperature $t = 10^\circ\text{C}$, and pressure 0.98×10^5 Pa.
- 6.11 Assuming that the gaskinetic radius of air molecules is 1.5×10^{-10} m, find the pressure under which a vacuum is attained in a Dewar flask (the separation between whose walls is 0.8 cm) at the temperature 290 K.
- 6.12 One end of an iron rod is maintained at the temperature 100°C , while the other is in contact with ice at 0°C . The cross-sectional area of the rod is 1 cm², its length being 20 cm. Find the mass of ice melted during 30 min assuming that the rod is thermally insulated, and hence the losses through its surface can be ignored.

ANSWERS

- 6.1. $v'' = 8.9 \times 10^{31}$ s⁻¹; $v' = 6.8 \times 10^9$ s⁻¹; $\langle l \rangle = 6.7 \times 10^{-8}$ m. 6.2. 1.73×10^{14} . 6.3. 0.135; 0.05; 0.006. 6.4. $p = 12$ Pa. 6.5. $l_{12} = 2.2 \times 10^{-5}$ m; $l_{21} = 9.6 \times 10^{-6}$ m. 6.6. 1.7×10^{-7} m; 1.1×10^{-10} m. 6.7. 1.78×10^{-5} Pa·s. 6.8. 1.5×10^{-10} m. 6.9. 1.48×10^{-5} m²/s; 1.85×10^{-5} Pa·s. 6.10. 13.2 mW/(m·K). 6.11. $p = 1.26$ Pa. 6.12. 5.25 g.

Appendix 1

SI Units Used in Molecular Physics

Quantity		Unit		
name of quantity	dimensionality	basic symbol	name of unit	symbol
Basic units				
Length	L	l	metre	m
Mass	M	m	kilogram	kg
Time	T	t	second	s
Electric current	I	I	ampere	A
Temperature	Θ	T	kelvin	K
Amount of substance	N	v	mole	mole
Luminous intensity	J	I	candela	cd
Derived units				
Velocity	LT^{-1}	v, u	metre per second	m/s
Acceleration	LT^{-2}	a	metre per second per second	m/s ²
Force	LMT^{-2}	F	newton	N
Pressure	$L^{-1}MT^{-2}$	p	pascal	Pa
Momentum	LMT^{-1}	p	kilogram-metre per second	kg·m/s
Energy	L^2MT^{-2}	W, E	joule	J
Power	L^2MT^{-3}	P	watt	W
Internal energy	L^2MT^{-2}	U	joule	J
Enthalpy	L^2MT^{-2}	H	joule	J
Free energy	L^2MT^{-2}	F	joule	J
Gibbs' function	L^2MT^{-2}	G	joule	J
Quantity of heat	L^2MT^{-2}	Q	joule	J
Work	L^2MT^{-2}	A	joule	J
Area	L^2	S	square metre	m ²
Volume	L^3	V	cubic metre	m ³
Molar volume	L^3N^{-1}	V_m	cubic metre per mole	m ³ /mole
Specific volume	L^3M^{-1}	v	cubic metre per kilogram	m ³ /kg
Density	ML^{-3}	ρ	kilogram per cubic metre	kg/m ³
Latent heat	L^2MT^{-2}	L	joule	J
Heat capacity	$L^2MT^{-2}\Theta^{-1}$	C	joule per kelvin	J/K

Appendix 1 (continued)

Entropy	$L^2MT^{-2}\Theta^{-1}$	S	joule per kelvin	J/K
Relative atomic mass	dimensionless	A_r		
Relative molecular mass	dimensionless	M_r		
Molar mass	MN^{-1}	M	kilogram per mole	kg/mole
Number of structural units of substance	dimensionless	n, ∞		
Concentration	L^{-3}	n_0	metre to minus	m^{-3}
Adiabatic exponent	dimensionless	γ	third power	
Polytropic exponent	dimensionless	n		
Efficiency	dimensionless	η		
Surface tension	MT^{-2}	σ	newton per metre	N/m
Osmotic pressure	$L^{-1}MT^{-2}$	Π	pascal joule	Pa
Chemical potential	L^2MT^{-2}	μ	joule	J
Compression ratio	$LM^{-1}T^2$	κ	inverse pascal	Pa^{-1}
Linear expansion coefficient	Θ^{-1}	α	inverse kelvin	K^{-1}
Volume expansion coefficient	Θ^{-1}	γ	inverse kelvin	K^{-1}
Temperature coefficient of pressure	Θ^{-1}	β	inverse kelvin	K^{-1}
Relative elongation	dimensionless	ϵ		
Relative shear	dimensionless	γ		
Young modulus	$L^{-1}MT^{-2}$	E	pascal	Pa
Normal stress	$L^{-1}MT^{-2}$	σ	pascal	Pa
Shear modulus	$L^{-1}MT^{-2}$	G	pascal	Pa
Tangential stress	$L^{-1}MT^{-2}$	τ	pascal	Pa
Poisson's ratio	dimensionless	μ		
Bulk modulus	$L^{-1}MT^{-2}$	K	Pascal	Pa
Mean free path	L	$\langle l \rangle, l$	metre	m
Collision frequency	T^{-1}	ν	inverse second	s^{-1}
Thermal conductivity	$LMT^{-3}\Theta^{-1}$	λ	watt per metre-kelvin	$W/(m \cdot K)$
Dynamic viscosity	$L^{-1}MT^{-1}$	η	pascal-second	$Pa \cdot s$
Diffusion coefficient	L^2T^{-1}	D	square metre per second	m^2/s

Appendix 2

Physical Constants*

Constant	Symbol	Numerical value
Velocity of light in vacuum	c	2.99792458×10^8 m/s
Acceleration due to gravity	g	9.80665 m/s ²
Normal molar volume	V_m	22.41383 m ³ /mole
Avogadro constant	N_A	6.022045×10^{23} mole ⁻¹
Loschmidt's number	N_L	2.686754×10^{25} m ⁻³
Boltzmann constant	k	1.380662×10^{-23} J/K
Planck constant	h	6.626176×10^{-34} J·Hz ⁻¹
	$\hbar$	$1.0545887 \times 10^{-34}$ J·s
Molar gas constant	R	8.31441 J/(mole·K)
Electric constant	ϵ_0	$8.85418782 \times 10^{-12}$ F/m
Magnetic constant	μ_0	$1.25663706144 \times 10^{-6}$ H/m
Atomic mass unit	m_u	$1.6605655 \times 10^{-27}$ kg
Stefan's constant	σ	5.67032×10^{-8} W/(m ² ·K ⁴)
Charge of electron	e	$1.6021892 \times 10^{-19}$ C
Rest mass of electron	m_e	9.109534×10^{-31} kg
Rest mass of proton	m_p	$1.6726485 \times 10^{-27}$ kg
Rest mass of neutron	m_n	$1.6749543 \times 10^{-27}$ kg
Gravitational constant	G	6.6720×10^{-11} m ³ /(kg·s ²)

* Fundamental physical constants GSSSDI-76.

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TO THE READER

MIR PUBLISHERS would be grateful for your comments on the content, translation and design of this book. We would also be pleased to receive any other suggestions you may wish to make.

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